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Appendix 5

Methods to Establish Baseline Air Quality Levels and Estimate Future Air Quality

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1 Introduction

This appendix discusses the methods used to estimate baseline and future air quality levels of important pollutants associated with the change from use of methyl tert-butyl ether (MTBE) based fuels to alternative fuels. Analyses were only done for the South Coast Air Basin (SoCAB), the most populated and most polluted air basin in California. Separate sections are included on data sources used, methods for establishing baseline levels, methods for estimating future air quality, and results.

2 Data Sources Used

The criteria pollutants studied included carbon monoxide (CO), nitrogen dioxide (NO_2), ozone (O_3), and particulate matter (PM_{10}). The key toxic air contaminants studied included ethanol, acetaldehyde, peroxyacetyl nitrate (PAN), MTBE, formaldehyde, benzene, and 1,3-butadiene. Some additional compounds were evaluated for baseline concentration but were dropped from further analysis because the potential differences in concentrations due to the use of different fuels relative to risk levels would not pose a significant health concern. Ambient data for criteria pollutants in 1996-1998 were used to represent the 1997 baseline to account for natural year-to-year meteorological fluctuations while only 1996-1997 toxics data were used to represent the 1997 baseline since 1998 data were not readily available at the time of data analysis. Data from before 1996 were not used because the fuels used then did not satisfy the requirements of California Phase 2 Reformulated Gasoline (RFG, also referred to as Cleaner Burning Gasoline).

Data from the following sources were used in our analysis:

- 1996-1998 Criteria Pollutant Monitoring Network in the SoCAB.
- 1996-1997 ARB Toxic Air Contaminant Network in the SoCAB (TAC data).
- 1996 SoCAB VOC Monitoring Study by Desert Research Institute (DRI data).
- 1996 Desert Research Institute Sepulveda Tunnel Study.
- 1996 and 1997 UC Berkeley Caldecott Tunnel Studies.
- 1997 ARB Emission Inventory for the SoCAB.

These data sets are described briefly below. Because Southern California Ozone Study 1997 (SCOS97) and Multiple Air Toxics Exposure Study (MATES) II data were not readily available at the time of data analysis, data from these studies were not included in our analysis. Although data from a 1999 UC Berkeley Tunnel Study were proposed to be used in the initial workplan, these data were not available at the time of our data analysis, and therefore also were not used.

2.1 Criteria Pollutant Monitoring Network

Criteria pollutants are those that have national or state ambient air quality standards. The Air Resources Board (ARB), in conjunction with local districts, operates a criteria pollutant monitoring network throughout California. Currently, there are thirty-one monitoring sites in the SoCAB, monitoring one or more of the pollutants included in our analysis. Further details regarding each monitoring site can be found in the ARB's State and Local Air Monitoring Network Plan (ARB, 1998a). Data from the statewide network are stored in the ARB's ambient air quality database, Aerometric Data Analysis and Management (ADAM). The 1996-1998 data used in our analysis were extracted from the ADAM database in July 1999 and were used to represent our baseline year of 1997. Hence, changes to data that may have occurred since that time would not be reflected in our analysis.

2.2 Toxic Air Contaminant (TAC) Monitoring Network

The California Air Resources Board operates a toxics sampling network, which consists of twenty-one monitoring sites throughout California. This network measures sixty-four pollutants including some of the compounds used in our analysis. Twenty-four-hour toxics samples are collected on a 1-in-12 day

basis. The sampling sites in the South Coast Air Basin are Burbank-West Palm Avenue, Los Angeles-North Main Street, North Long Beach, Riverside-Rubidoux, and Upland. Both 1996 and 1997 TAC data used in this study were extracted in December 1998 from the ARB's database and stored on a CD-ROM available to the public (ARB, 1998b). 1998 data were not available in time to use in our analysis. The exception is data for MTBE, which were not on the CD-ROM and were extracted in July 1999.

2.3   Desert Research Institute Study

Zielinska et al. (1999) at Desert Research Institute (DRI) undertook a study entitled "Air Monitoring Program for Determination of the Impacts of the Introduction of California Phase 2 Reformulated Gasoline on Ambient Air Quality in the South Coast Air Basin" in 1995-1996. The objective of this study was to conduct ambient measurements of speciated hydrocarbons, oxygenated organic gases, methane, carbon monoxide, and carbon dioxide during the summers of 1995 and 1996 in the South Coast Air Basin for providing data required to determine air quality impacts of the reformulated gasoline. In the study, samples were collected from two source-dominated sites (downtown LA at North Main and Burbank), a downwind receptor site (Azusa), and a background site (Santa Monica) for forty-two days (six weeks) throughout the summers (i.e. from July to the end of September) of 1995 and 1996. Two three-hour samples were taken per sampling day, one in the morning (AM) during rush hour traffic and one in the afternoon (PM). Results for 1996 were used in our analysis.

2.4   Los Angeles Sepulveda Tunnel Study

Gertler et al. (1997) at DRI conducted an impact study of California Phase 2 Reformulated Gasoline at the Los Angeles Sepulveda Tunnel in 1995-1996. The objectives of this study were to quantify automotive emission rates of CO, NMHC, speciated hydrocarbons, NO_X, and CO_2 following the introduction of California Phase 2 RFG program and to compare the 1996 results with the 1995 results to assess the impact of RFG. The Sepulveda Tunnel runs under part of the Los Angeles International Airport (LAX). Eighteen sampling experiments were performed in 1996 over the period of July 23 to July 25 from 6 AM to 8 PM. One-hour samples were collected at both ends of the tunnel and analyzed for CO, NMHC, various hydrocarbon species, and NO_x. Results from 17 of the 18 sampling experiments were reported by DRI and used in our analysis.

2.5   Bay Area Caldecott Tunnel Study

Kirchstetter et al. (Kirchstetter and Harley, 1999a; Kirchstetter et al., 1999b) at the University of California at Berkeley performed a similar RFG air quality impact study at the Caldecott tunnel, east of San Francisco Bay on State Highway 24, during the summers of 1994 through 1997. The tunnel was heavily used during commute hours. In the study, two-hour integrated air samples were collected for analyzing speciated hydrocarbon and carbonyls during the afternoon commute period (1600 to 1800). On selected days, additional measurements were also performed earlier in the afternoon. Concentrations of CO_2, CO, and NO_x were measured continuously and each was recorded as a five-minute average concentration. The data collected from 1996 and 1997 were used in our analysis.

2.6   Emission Inventory Data

Emission inventories representing summer emissions in 1997 and 2003 for the South Coast Air Basin were extracted from the California Emission Forecasting System (CEFS) by the ARB's Emission Inventory Branch (ARB, 1999) in late May 1999 for the ARB's modeling staff. The modeling staff speciated the hydrocarbon data and provided summer inventories for our analysis. Additionally, 1997 annual and winter emission inventories were extracted from CEFS in late July 1999. The development of these data is discussed in a separate appendix.

3   Establishing Baseline Air Quality Levels

3.1   Criteria Pollutants

The criteria pollutants evaluated in this study were carbon monoxide, nitrogen dioxide, ozone and particulate matter (PM_{10}). Baseline levels to represent 1997 were based on 1996-1998 data drawn from the ARB's ADAM database.

3.1.1   Carbon Monoxide

The maximum measured one-hour and eight-hour concentrations over the 1996-1998 period were 22.5 and 17.5 ppm, respectively. Both were measured at the Lynwood monitoring station.

3.1.2   Nitrogen Dioxide

The maximum measured one-hour and daily average concentrations over the 1996-1998 period were .255 and .117 ppm, respectively. The one-hour maximum was measured at the Banning monitoring station and the maximum daily average concentration was measured at the Los Angeles-North Main monitoring station. A maximum annual-average concentration of .043 ppm was measured at the Pomona monitoring station.

3.1.3   Ozone

The maximum measured one-hour and eight-hour concentrations over the 1996-1998 period were .244 and .206 ppm, respectively. Both were measured at the Lake Gregory monitoring station.

3.1.4   Particulate Matter (PM_{10})

The maximum measured daily average concentration over the 1996-1998 period was 227 : g/m^3, measured at the Banning monitoring station. The maximum annual geometric mean concentration of 56 : g/m^3 was measured at the Riverside-Rubidoux monitoring station.

3.2   Toxic Pollutants

The toxics pollutants evaluated in our analysis included benzene, 1,3-butadiene, MTBE, acetaldehyde, formaldehyde, toluene, and xylene. Isobutene and n-hexane are also discussed in this section because estimates for these two compounds involve the same analytical procedures. Baseline pollutant levels to represent 1997 were based on 1996-1997 data drawn from the ARB's toxics database, from DRI data, and from correlation analyses using these same data, tunnel study results and criteria pollutant data. Different approaches were used for different groups of toxics compounds.

3.2.1   Benzene, 1,3-Butadiene and MTBE

Two different approaches were used to estimate benzene, 1,3-butadiene, and MTBE levels representative of 1997. First, we used measured concentrations directly from the toxics sampling network. In addition, we developed ratios between these toxic compounds and carbon monoxide and used them to estimate levels at locations where there were no direct toxics measurements, but there were CO measurements. This latter approach allowed us to estimate pollutant concentrations at nineteen locations, rather than the five locations for which toxics sampling data are available. The two approaches provide a range in estimates. The next section describes how we developed the ratios used in the latter approach.

3.2.1.1   Development of Ratios between Toxic Compounds and CO

To estimate toxics levels at locations other than those where toxics compounds are sampled, we developed ratios between toxics compounds and CO. The general procedure for determining the ratio between a TAC and CO is described below. The same procedure was applied to all TACs except the aldehydes.

The first step was to extract the TAC and CO data from the aforementioned data sets and select sites where both TACs and CO were measured. CO was not measured at the Upland site (one of five sites in the TAC monitoring network in the SoCAB) in 1996 or 1997, so data collected at Upland were not used in the subsequent calculations. As for the DRI data set, both the AM data and the combined AM plus PM data were analyzed separately in this study to consider possible differences between the morning period of direct source contribution and overall behavior during the day.

Then, we estimated representative background concentrations and subtracted them from the extracted data. The background subtraction was to facilitate development of a single basin-wide ratio between a TAC and CO. Because there was no significant natural sources for the toxics compounds studied (except aldehydes), atmospheric background for each TAC was determined to be negligible (zero). However, for CO the background was estimated to be 100 ppb, based on measurements at Santa Catalina, Point Conception, and San Nicholas Island.

The next step was to exclude values below the level of detection (LOD) and some outliers because such values could distort the ratios being calculated. For the TAC monitoring network data set, for example, 19 benzene data values and two CO data values (out of 109 pairs of matched data values collected in the SoCAB in 1996) were below their LOD values. As for outliers, two exceptionally high benzene values, observed on July 7 1996 (AM) and July 8 1996 (PM) in the DRI data, were also excluded in subsequent calculations.

Finally, a least-squares linear regression technique was applied to the TAC and CO data and the regression line forced through the origin. Then, the TAC to CO ratios and correlation coefficients were calculated.

The specific application of these procedures to develop ratios to CO for benzene, butadiene, and MTBE are discussed further below.

3.2.1.1.1   Benzene

Table 1 summarizes the ratios and correlation coefficients between benzene and CO derived from the five data sets. Ratios calculated from the emissions data were based on ratios of benzene emissions to CO emissions estimated for all sources and for just on-road sources, respectively. In general, good correlation between benzene and CO data was observed, except for the 1997 Caldecott data set. No significant difference in ratios was observed between the DRI AM and AM plus PM data sets. Except those derived from the Caldecott data sets, the benzene to CO ratios range from 0.81 to 1.21 (ppb/ppm). Statewide ratios between benzene and CO derived from TAC data collected throughout the state in 1996 and 1997 are 1.03 and 0.88 (ppb/ppm), respectively. A ratio of 1.0 (ppb/ppm) was selected as a reasonable ratio of benzene to CO.

Figure 1 shows a scatterplot of benzene versus CO for the South Coast TAC samples collected in 1996. Data collected in different sites are represented by different symbols. Scatterplots of benzene versus CO for the DRI data and the Sepulveda tunnel data are shown in Figures 2 and 3, respectively.

3.2.1.1.2   1,3-Butadiene

Table 2 summarizes the ratios and correlation coefficients for 1,3-butadiene to CO derived from the aforementioned data sets. Good correlation between butadiene and CO was observed for all data sets except the two tunnel studies and Riverside data. The ratios range from 0.22 to 0.34 (ppb/ppm), except those obtained from Caldecott tunnel data. Statewide ratios calculated from TAC data collected throughout the state in 1996 and 1997 are 0.29 and 0.28 (ppb/ppm), respectively. A ratio of 0.30 (ppb/ppm) was selected as a reasonable ratio of butadiene to CO. Scatterplots of 1,3-butadiene versus CO are presented in Figures 4, 5, and 6 for 1996 TAC data, DRI data, and Sepulveda tunnel data, respectively.

Table 1. Summary of Linear Regression Parameters for Correlations between Ambient Levels of Benzene and CO[a].

	TAC Network		DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventory[b]	
	Ratio	R^2	Ratio	R^2	Ratio	R^2	Ratio	R^2	All Sources	On-road Sources
1996										
California Statewide[c]	1.03	0.61								
South Coast Air Basin[c]	0.90	0.76	1.10	0.93	1.11	0.91			1.21	1.18
Burbank	0.86	0.66	1.14	0.98	1.14	0.98				
Los Angeles	0.84	0.92	1.03	0.89	1.05	0.90				
Long Beach	1.13	0.81								
Riverside	0.98	0.69								
Azusa			1.17	0.95	1.19	0.86				
Sepulveda Tunnel							1.10	0.96		
Caldecott Tunnel							0.59	0.76		
1997										
California Statewide[c]	0.88	0.82								
South Coast Air Basin[c]	0.80	0.89								
Burbank	0.78	0.84								
Los Angeles	0.82	0.95								
Long Beach	0.81	0.88								
Caldecott Tunnel							0.53	0.46		

a. Concentration units are ppmv for CO and ppbv for benzene. CO background of 100 ppb was subtracted in CO measurements.
   Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.
b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.
c. Statewide and basin-wide ratios and correlation coefficients were calculated using the data collected statewide and in the SoCAB, respectively.

Four TAC Sites, 1996

Figure 1. Benzene vs CO for SoCAB (Four TAC Sites, 1996).

SoCAB (Three DRI Sites, 1996)
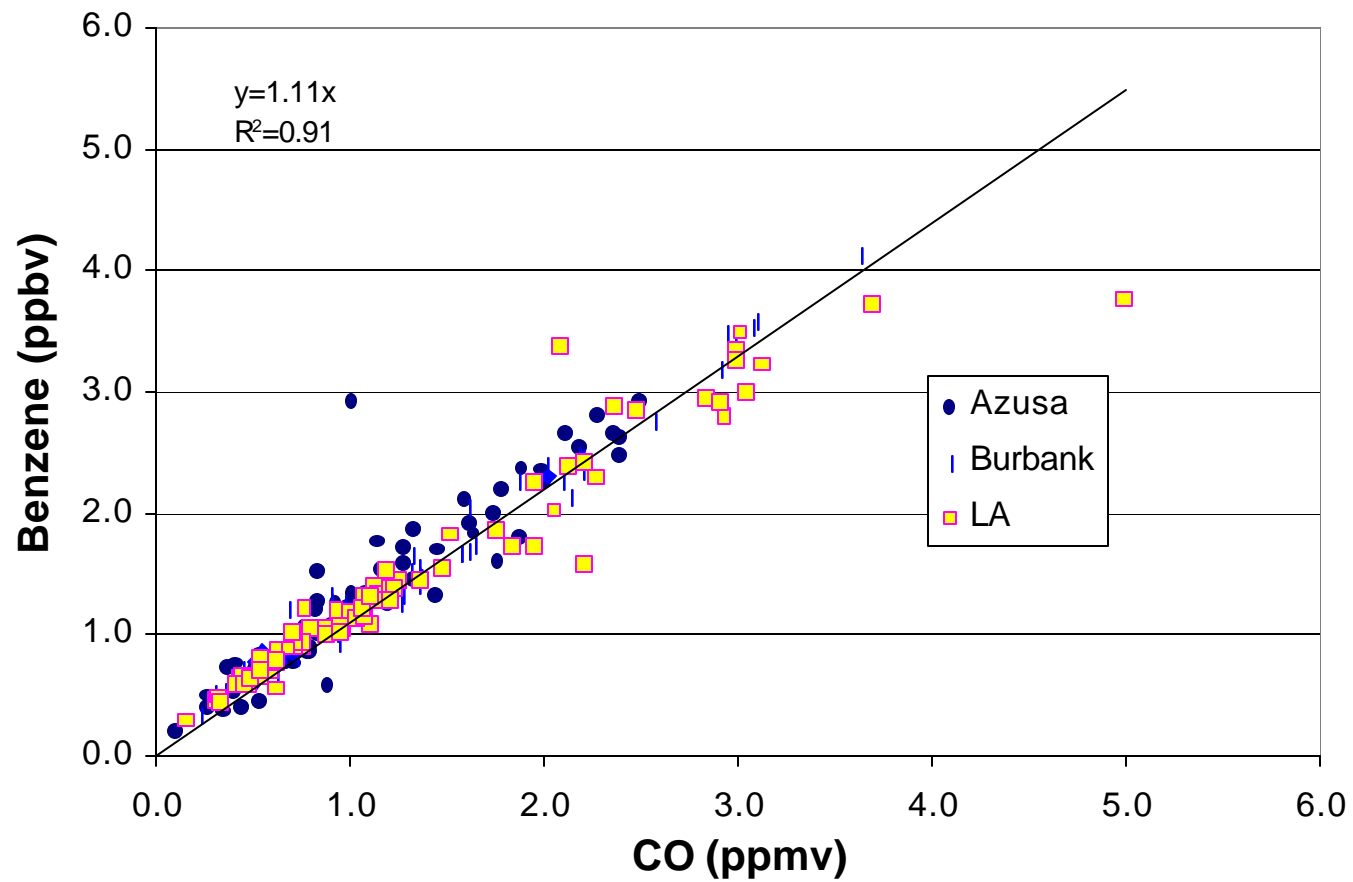
Figure 2. Benzene vs CO for SoCAB (Three DRI Sites, 1996).

LA Sepulveda Tunnel (1996)

Figure 3. Benzene vs CO for LA Sepulveda Tunnel (1996).

Table 2. Summary of Linear Regression Parameters for Correlations between Ambient levels of 1,3-Buadiene and of CO[a].

	TAC Network		DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventory[b]	
	Ratio	R^2	Ratio	R^2	Ratio	R^2	Ratio	R^2	All Sources	On-road Sources
1996										
California Statewide[c]	0.29	0.79								
South Coast Air Basin[c]	0.27	0.84	0.26	0.76	0.24	0.71			0.33	0.32
Burbank	0.26	0.85	0.26	0.78	0.23	0.72				
Los Angeles	0.27	0.90	0.25	0.68	0.24	0.72				
Long Beach	0.34	0.68								
Riverside	0.26	0.46								
Azusa			0.27	0.83	0.22	0.64				
Sepulveda Tunnel							0.24	0.57		
Caldecott Tunnel							0.13	0.02		
1997										
California Statewide[c]	0.28	0.81								
South Coast Air Basin[c]	0.28	0.82								
Burbank	0.25	0.84								
Los Angeles	0.30	0.90								
Long Beach	0.30	0.74								
Caldecott Tunnel							0.15	0.28		

a. Concentration units are ppmv for CO and ppbv for 1,3-butadiene. CO background of 100 ppb was subtracted in CO measurements.
   Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.
b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.
c. Statewide and basin-wide ratios and correlation coefficients were calculated using the data collected statewide and in the SoCAB, respectively.

SoCAB (Four TAC Sites, 1996)
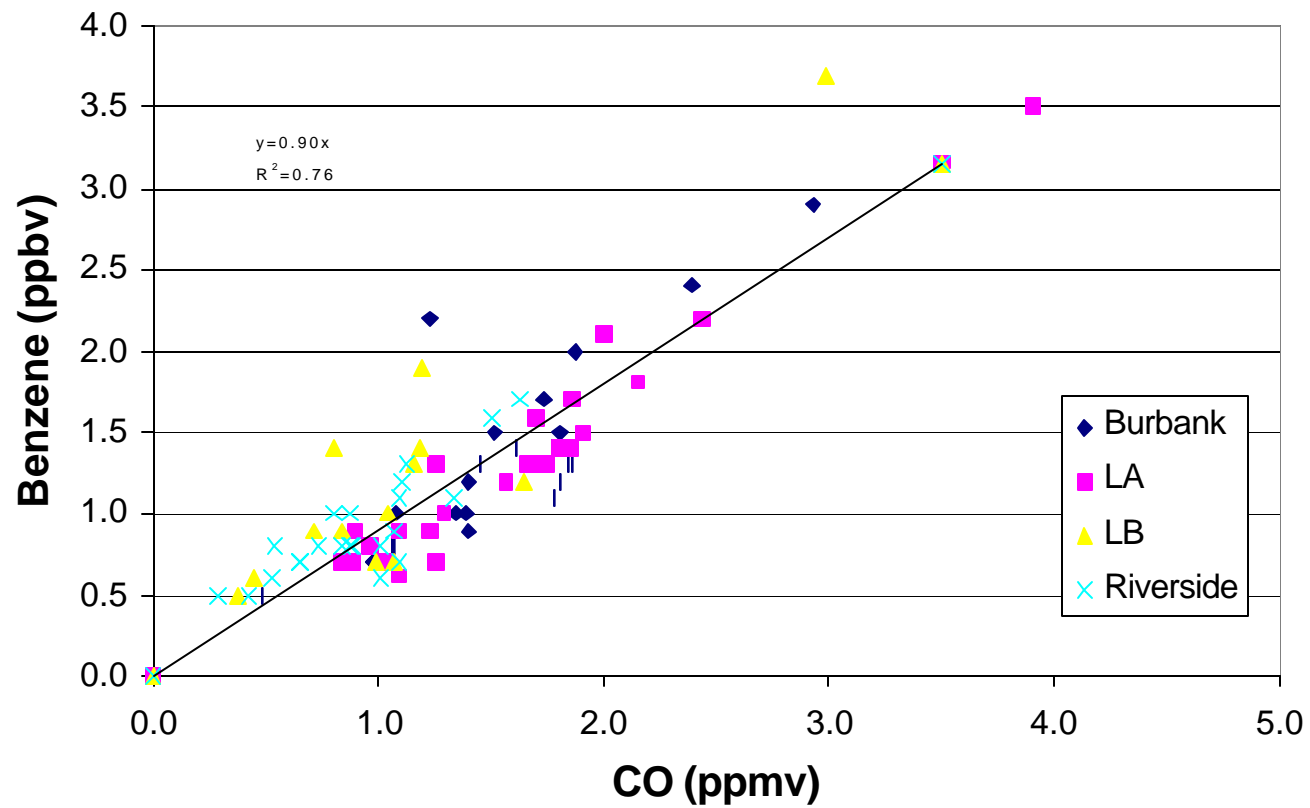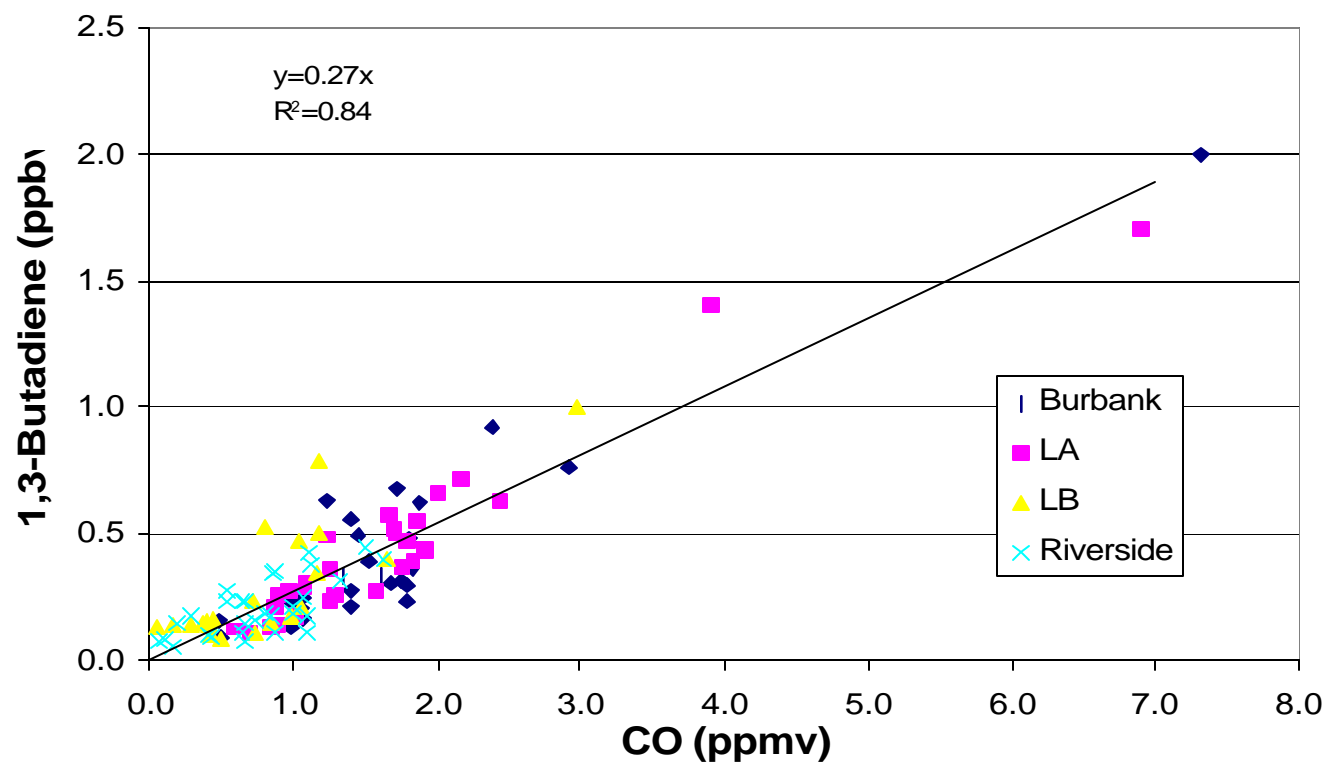

Figure 4. 1,3-Butadiene vs CO for SoCAB (Four TAC Sites, 1996).

SoCAB (Three DRI Sites, 1996)
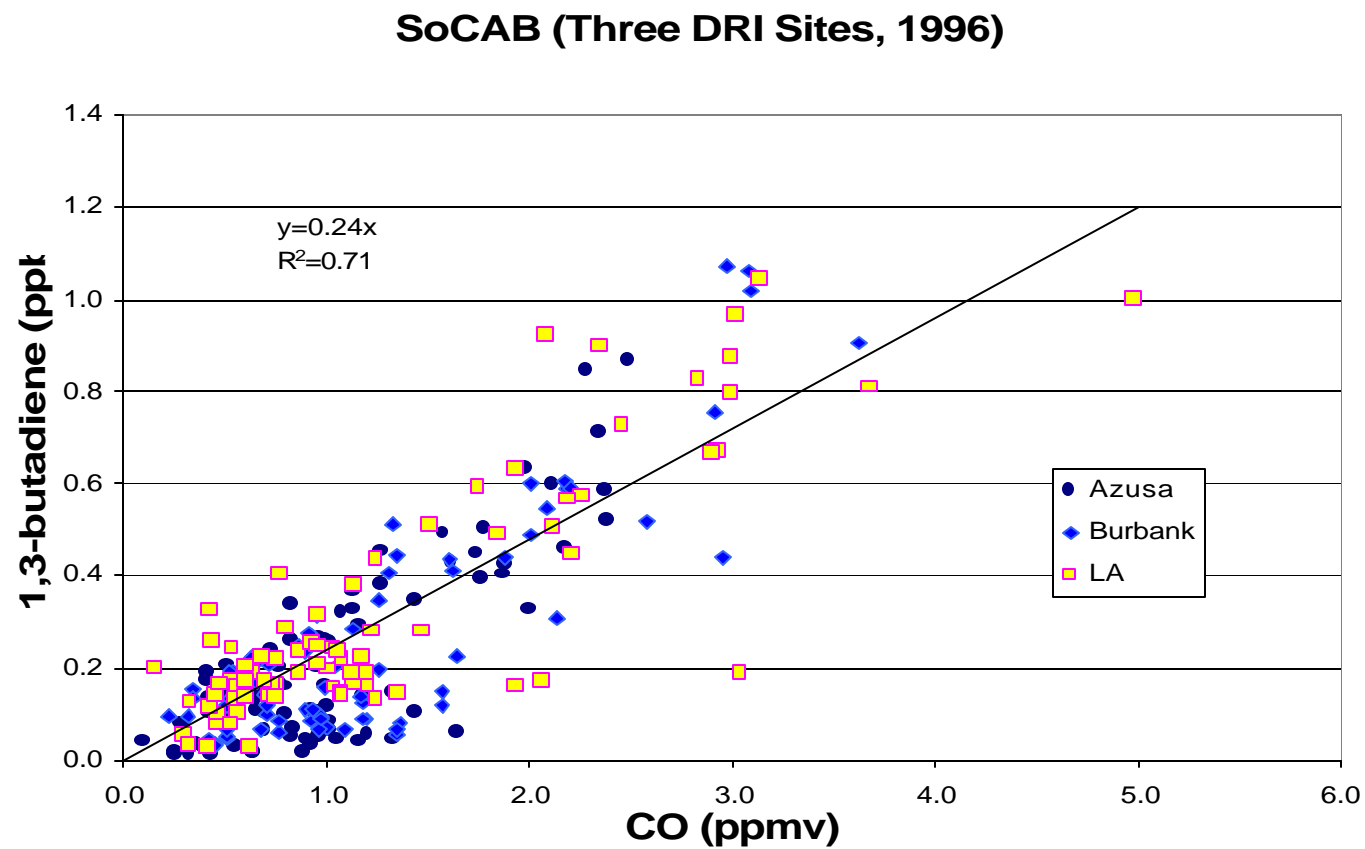
Figure 5. 1,3-Butadiene vs CO for SoCAB (Three DRI Sites, 1996).
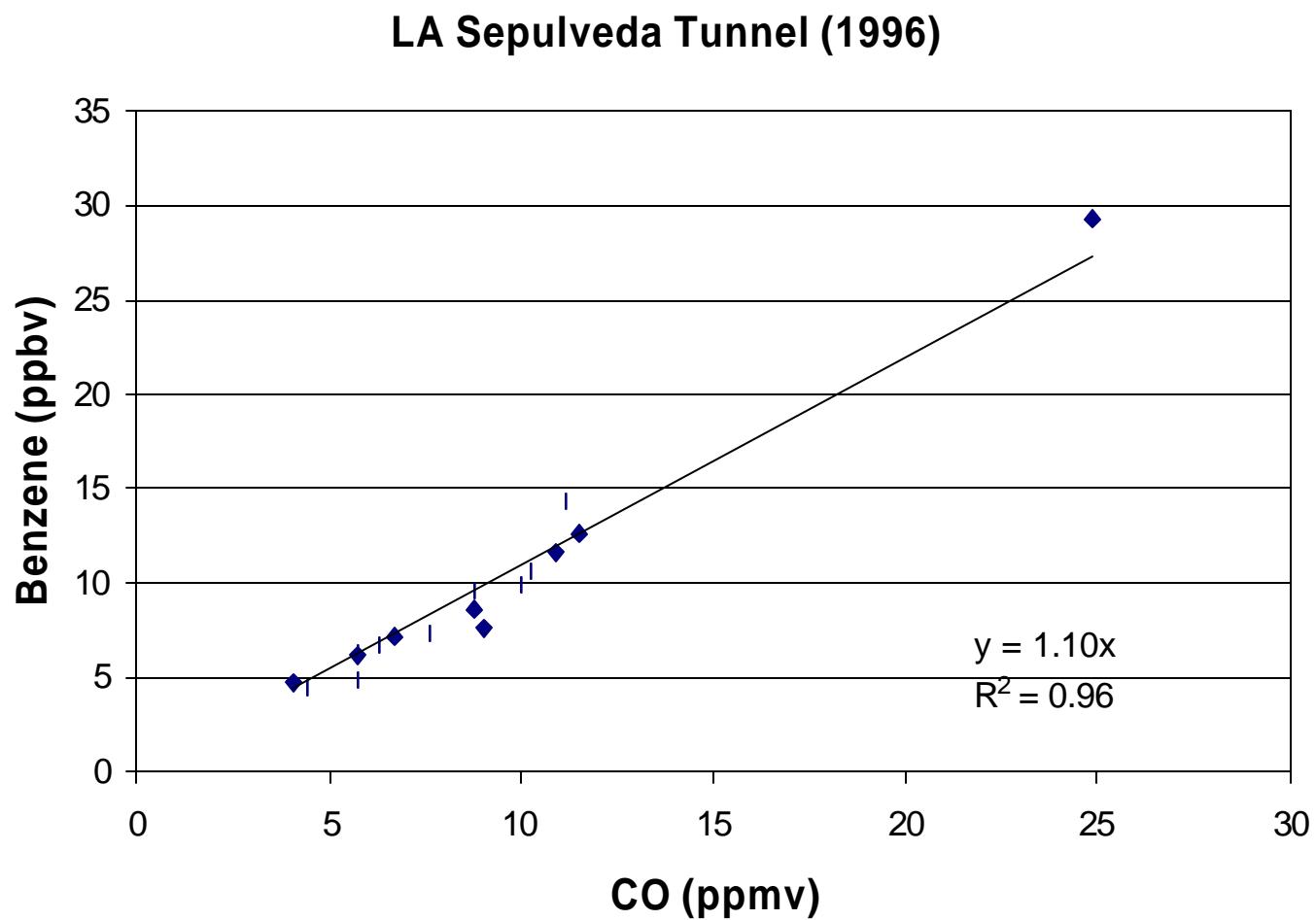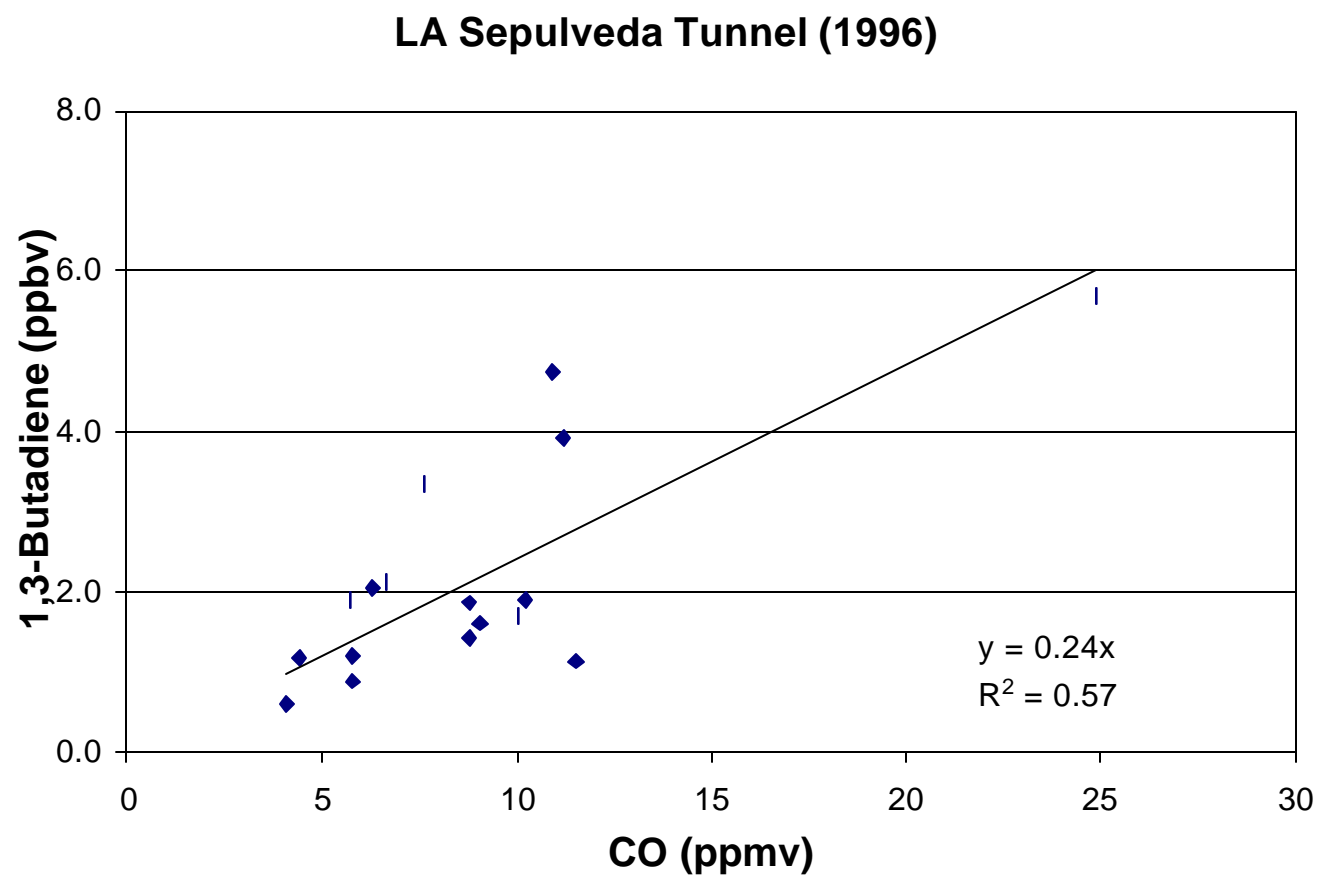
Figure 6. 1,3-Butadiene vs CO for LA Sepulveda Tunnel (1996)

3.2.1.1.3   MTBE

Table 3 summarizes the ratios and correlation coefficients for MTBE to CO derived from the same data sets described above. Good correlation was observed for the DRI data set and the 1997 TAC data. However, correlation was poor for the Caldecott tunnel data and the 1996 Long Beach data. The ratios obtained from the TAC network data and the DRI data range from 2.6 to 4.6 (ppb/ppm), while the ratios derived from emission inventory and tunnel data are substantially lower. Based on these results, a ratio of 3.0 (ppb/ppm) was selected as a reasonable ratio of MTBE to CO. Scatterplots of MTBE versus CO are shown in Figures 7, 8, and 9 for 1996 TAC data, DRI data, and Sepulveda data, respectively.

3.2.1.2   Estimated 1997 Concentrations

3.2.1.2.1   Maximum Daily Average

The maximum measured daily average benzene concentration in the South Coast Air Basin from 1996 to 1997 was 7.4 ppb, measured at Burbank on 1/10/96. The maximum measured daily average CO concentration in the South Coast Air Basin between 1996 and 1998 was 9.6 ppm, measured at Lynwood on 11/1/97. Multiplying this by the benzene to CO ratio of 1.0 (ppb/ppm), the estimated maximum daily average benzene concentration at Lynwood is 9.6 ppb.

The maximum measured daily average 1,3-butadiene concentration in the South Coast Air Basin from 1996 to 1997 was 2.0 ppb, measured at Burbank on 1/10/96. Multiplying the maximum daily average CO concentration (9.6 ppm) by the butadiene to CO ratio of 0.3 (ppb/ppm), the estimated maximum daily average butadiene concentration at Lynwood is 2.9 ppb.

The maximum measured daily average MTBE concentration in the South Coast Air Basin from 1996 to 1997 was 13 ppb, measured at Burbank on 11/24/97.   Multiplying the maximum daily average CO concentration (9.6 ppm) by the MTBE to CO ratio of 3.0 (ppb/ppm), the estimated maximum daily average MTBE concentration at Lynwood is 29 ppb.

3.2.1.2.2   Maximum One-hour Average

The maximum measured daily average benzene concentration in the South Coast Air Basin from 1996 to 1997 was 7.4 ppb, measured at Burbank on 1/10/96. The corresponding maximum one-hour and daily average CO concentrations at Burbank on this day were 11.6 ppm and 7.43 ppm, respectively. Assuming that benzene concentrations vary during the day in proportion to CO concentrations (since they are both primarily emitted by motor vehicles and affected by the same meteorology), the estimated maximum one-hour benzene concentration at Burbank is 11.6 ppb. The maximum measured one-hour average CO concentration in the South Coast Air Basin between 1996 and 1998 was 22.5 ppm, measured at Lynwood on 1/6/96. Multiplying this by the benzene to CO ratio of 1.0 (ppb/ppm), the estimated maximum benzene concentration at Lynwood is 22.5 ppb.

The maximum measured daily average butadiene concentration in the South Coast Air Basin from 1996 to 1997 was 2.0 ppb, measured at Burbank on 1/10/96. The corresponding maximum one-hour and daily average CO concentrations at Burbank on this day were 11.6 ppm and 7.43 ppm, respectively. Assuming that butadiene concentrations vary during the day in proportion to CO concentrations (since they are both primarily emitted by motor vehicles and affected by the same meteorology), the estimated maximum one-hour butadiene concentration at Burbank is 3.1 ppb. Multiplying the maximum one-hour average CO concentration (22.5 ppm) by the butadiene to CO ratio of 0.3 (ppb/ppm), the estimated maximum butadiene concentration at Lynwood is 6.8 ppb.

Table 3. Summary of Linear Regression Parameters for Correlations between Ambient Levels of MTBE and Those of CO[a]

	TAC Network		DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventory[b]	
	Ratio	R^2	Ratio	R^2	Ratio	R^2	Ratio	R^2	All Sources	On-road Sources
1996										
South Coast Air Basin[c]	2.90	0.59	4.06	0.84	4.13	0.83			1.82	2.31
Burbank	3.07	0.71	4.56	0.96	4.61	0.95				
Los Angeles	2.66	0.72	3.43	0.81	3.51	0.84				
Long Beach	3.37	0.10								
Riverside										
Azusa			4.45	0.90	4.59	0.79				
Sepulveda Tunnel							2.28	0.93		
Caldecott Tunnel							0.88	0.35		
1997										
South Coast Air Basin[c]	3.00	0.88								
Burbank	3.25	0.90								
Los Angeles	2.59	0.93								
Long Beach	3.12	0.91								
Caldecott Tunnel							0.62	0.33		

a. Concentration units are ppmv for CO and ppbv for MTBE. CO background of 100 ppb was subtracted in CO measurements.
   Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.
b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.
c. Basin-wide ratio and correlation coefficient were calculated using the data collected in the SoCAB.
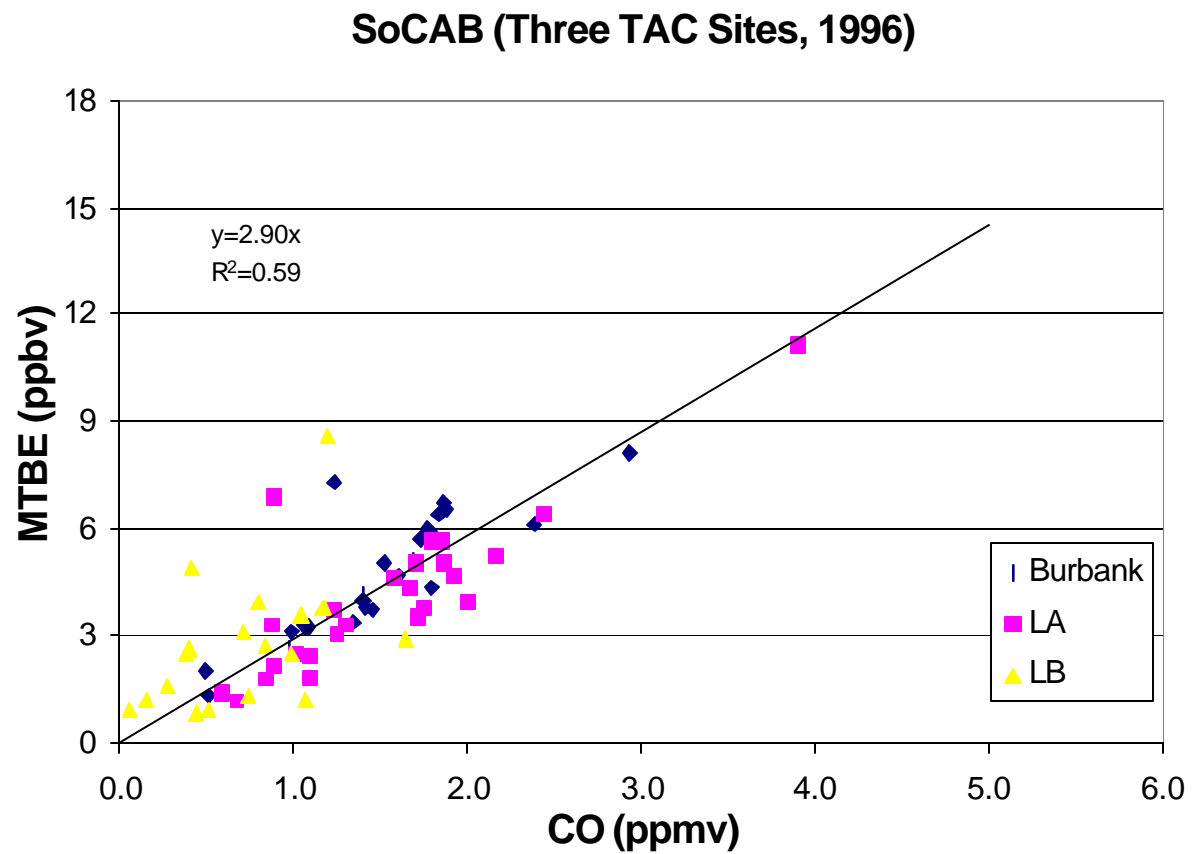
Figure 7. MTBE vs CO for SoCAB (Three TAC Sites, 1996).

SoCAB (Three DRI Sites, 1996)
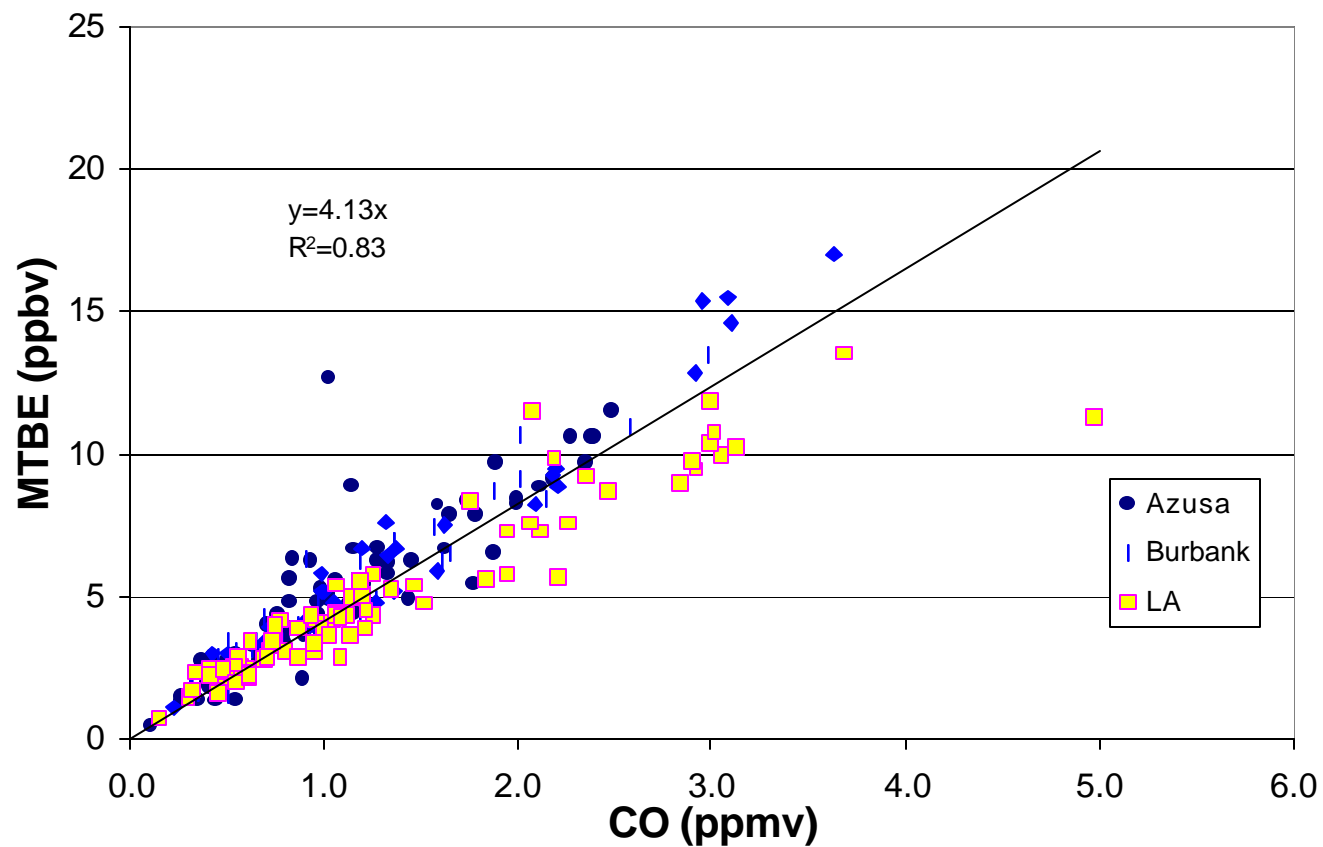
Figure 8. MTBE vs CO for SoCAB (Three DRI Sites, 1996).

LA Sepulveda Tunnel (1996)

y = 2.28x

$R^2 = 0.93$

MTBE (ppbv)

CO (ppmv)
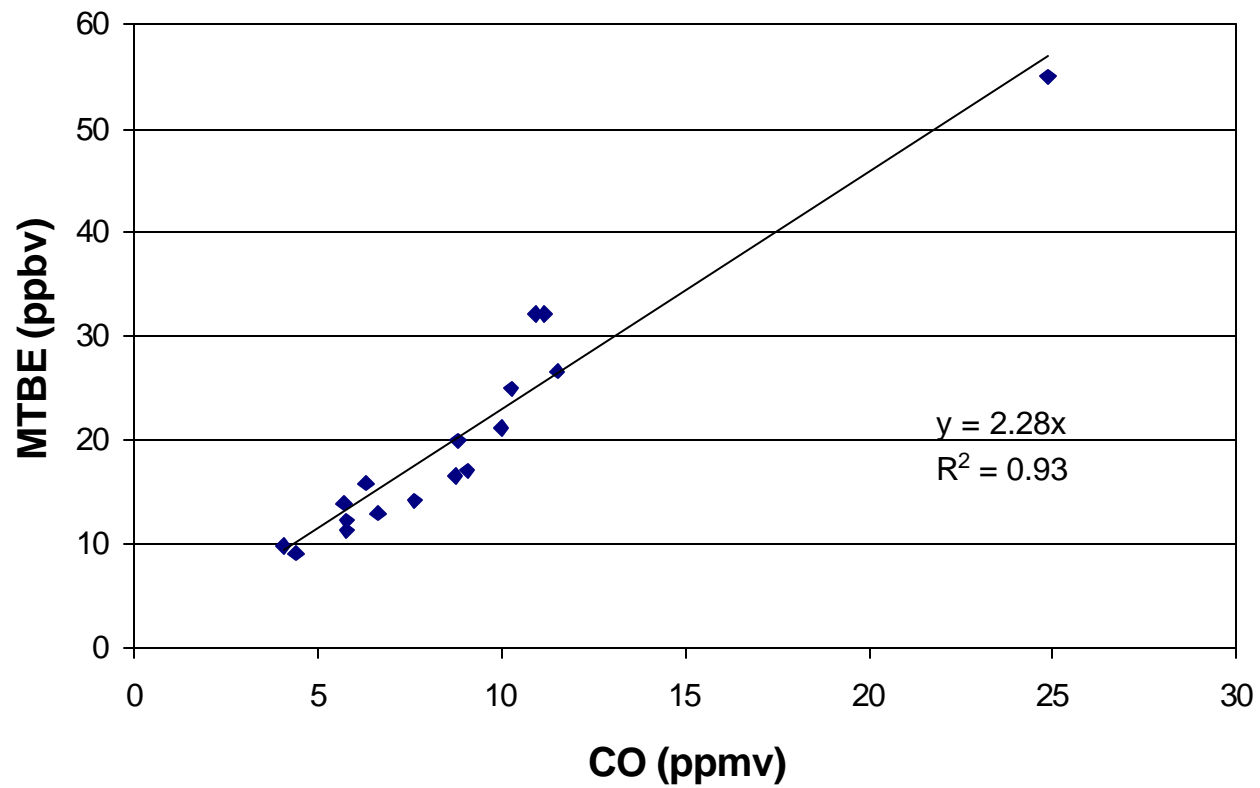
Figure 9. MTBE vs CO for LA Sepulveda Tunnel (1996).

The maximum measured daily average MTBE concentration in the South Coast Air Basin from 1996 to 1997 was 13 ppb, measured at Burbank on 11/24/97. The corresponding maximum one-hour and daily average CO concentrations at Burbank on this day were 5.9 ppm and 4.03 ppm, respectively. Assuming that MTBE concentrations vary during the day in proportion to CO concentrations (since they are both primarily emitted by motor vehicles and affected by the same meteorology), the estimated maximum one-hour MTBE concentration at Burbank is 19 ppb. Multiplying the maximum one-hour average CO concentration (22.5 ppm) by the MTBE to CO ratio of 3.0 (ppb/ppm), the estimated maximum MTBE concentration at Lynwood is 68 ppb.

3.2.1.2.3   *Population Weighted Annual Exposure*

In calculating health risks, the Office of Environmental Health Hazard Assessment (OEHHA) uses population weighted annual pollutant exposure as an indicator of the concentration to which a typical person is exposed to toxic substances. For benzene, butadiene, and MTBE, population weighted annual-average exposure was calculated two ways.

The first way used available data from the five toxics monitoring sites in the South Coast Air Basin. Annual-averages for 1996 and 1997 were averaged for the individual monitoring sites. Then the population weighted annual-average concentration was estimated by interpolating between the five monitoring sites using a previously developed technique (ARB, 1993). This interpolation process starts with population data by census tract and an associated centroid. Then data for any monitoring site within 50 kilometers of the centroid is used in determining a representative concentration to which people in the census tract are exposed. In determining this representative concentration, the contribution from each monitoring site is weighted in proportion to the inverse of the square of the distance from the population centroid to the monitoring site. To determine the population weighted exposure, the population of individual census tracts is multiplied by their representative concentration, summed over all census tracts and then divided by the total population across all census tracts. The resulting population weighted annual-average concentrations calculated to represent the SoCAB in 1997 were 1.1 ppb for benzene, 0.34 ppb for 1,3-butadiene, and 3.9 ppb for MTBE, respectively.

The second way used an average of annual-average CO concentrations for 1996-1998 to calculate benzene, 1,3 butadiene and MTBE concentrations at nineteen monitoring locations in the South Coast Air Basin using the ratios to CO described in Section 3.2.1.1. Population weighted annual-average concentrations of 1.2 ppb benzene, 0.36 ppb butadiene, and 3.6 ppb MTBE were calculated using the interpolation and averaging procedure described in the paragraph above.

3.2.2   Acetaldehyde and Formaldehyde

Three different approaches were considered in estimating acetaldehyde and formaldehyde levels representative of 1997. First was the use of measured concentrations directly from the toxics sampling network. Second was the use of results from the air quality model simulations. Third was developing relationships between aldehydes and CO and oxidant so aldehyde values could be estimated at many more locations than are sampled with the toxics monitoring network. Our attempt to correlate aldehydes with CO and oxidant was not considered sufficiently reliable and was abandoned. A brief discussion of that effort is presented in Section 3.2.2.2.

3.2.2.1   Estimated 1997 Concentrations

3.2.2.1.1   *Maximum Daily Average*

The maximum measured daily average acetaldehyde level in the South Coast Air Basin from 1996 to 1997 was 5.1 ppb, measured at Upland on 8/13/96. The maximum measured daily average formaldehyde level in the South Coast Air Basin from 1996 to 1997 was 14.0 ppb, measured at Upland on 8/13/96. In addition, the regional air quality model simulation for 1997 predicted the basin-wide maximum acetaldehyde and formaldehyde concentrations to be 6.2 ppb and 11.4 ppb, respectively.

Since the maximum formaldehyde concentration predicted is lower than the maximum measured value, we considered the measured value to be more representative of the maximum level.

3.2.2.1.2   *Maximum One-hour Average*

The maximum one-hour aldehyde concentrations were estimated three ways using three data sources.

First, three-hour DRI data were used as a basis. The maximum three-hour acetaldehyde concentration measured was 13.88 ppb at Azusa on 8/28/96 between 1300 and 1600 PDT. Corresponding three-hour and maximum one-hour ozone values for this period are 0.11 and 0.14 ppm. Assuming that acetaldehyde concentrations vary in the afternoon in proportion to ozone concentrations (since both are strongly influenced by atmospheric chemical reactions at this time of day), the estimated maximum one-hour acetaldehyde concentration at Azusa is 17.7 ppb.   Similarly for formaldehyde, the maximum 3-hour measurement of 18.17 ppb was in the afternoon on 8/29/96 in Burbank. The corresponding estimated one-hour maximum is 20.3 ppb.

Second, TAC daily average data were used. The maximum daily average acetaldehyde level at Upland, measured on 8/13/96, was 5.1 ppb. The average ratio of maximum one-hour average to daily average ozone for monitors operating in the South Coast Air Basin on 8/13/96 was 2.7. Assuming that acetaldehyde concentrations at Upland in August vary in proportion to ozone levels (photochemical model simulations indicate that over 90% of the acetaldehyde and 85% of the formaldehyde at Upland is from atmospheric chemical reactions on high ozone days), the maximum one-hour acetaldehyde concentration estimated for Upland is 13.8 ppb. Similarly, the maximum daily average formaldehyde level at Upland, measured on 8/13/96, was 14 ppb and the corresponding estimated maximum one-hour concentration is 37.8 ppb.

Third, the regional air quality model simulation for 1997 predicted the basin-wide maximum acetaldehyde and formaldehyde concentrations to be 9.2 ppb and 22.7 ppb, respectively. Since the model maximum one-hour concentration of 9.2 ppb acetaldehyde was less than the maximum three-hour concentration measured value, we considered the estimates made using the measured values to be more representative of maximum levels.

3.2.2.1.3   *Population Weighted Annual Exposure*

There are five monitoring sites in the SoCAB at which acetaldehyde and formaldehyde measurements were made between 1996 and 1997. The population weighted annual-average concentrations were calculated using the interpolation and averaging procedure described in Section 3.2.1.2.3 above. The resulting population weighted annual-average concentrations calculated to represent the SoCAB in 1997 are 1.75 ppb for acetaldehyde and 4.65 ppb for formaldehyde.

3.2.2.2   Attempt to Correlate Aldehydes with CO and Oxidant

To provide a broader base of data for estimating aldehyde concentrations, an attempt was made to correlate acetaldehyde and formaldehyde concentrations with carbon monoxide and oxidant (O_3+NO_2) concentrations. CO was used as an index of primary aldehyde emissions and oxidant as an index of the secondary aldehyde produced through chemical reactions in the atmosphere. To develop a relationship with CO, we plotted aldehydes vs. CO using both the TAC data and 6 to 9 am data for 1996 from the DRI study. Because some of the measured acetaldehyde and formaldehyde may be secondary in origin, we opted to estimate a ratio between primary aldehydes and CO by plotting the aldehyde to CO ratio vs. CO and identifying the minimum ratio that generally had most if not all of the points above it. For formaldehyde from the toxics monitoring network, the minimum ratio was 1.4 ppb/ppm CO (see Figure 10). For DRI formaldehyde data, the minimum ratio was 2.1 (see Figure 11). For acetaldehyde, the minimum ratio was 0.50 (see Figure 12) for TAC for and 0.95 (see Figure 13) for the DRI data. In developing these minimum ratios we subtracted background levels
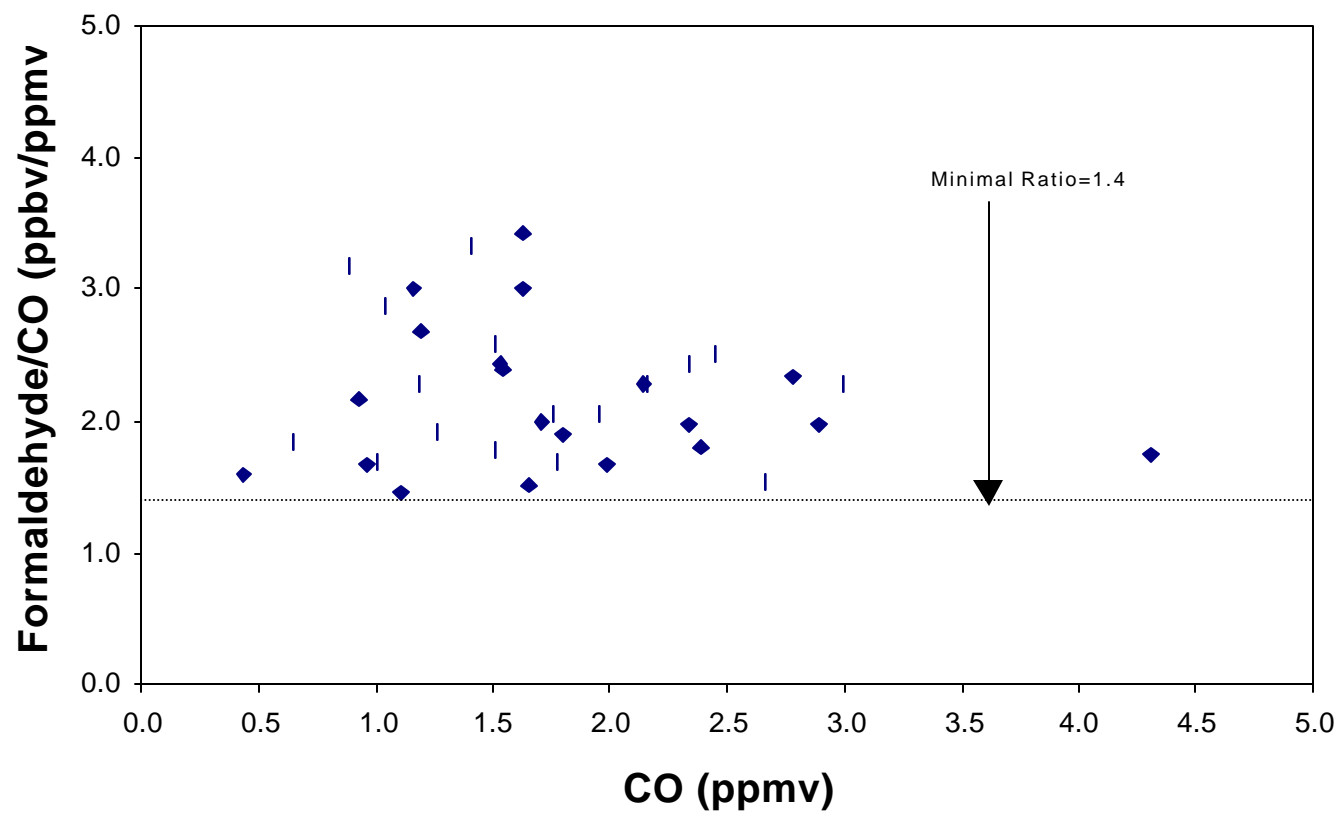
Figure 10. Formaldehyde/CO Ratio versus CO for SoCAB (TAC Winter Data, 1996 and 1997).

SoCAB (Three DRI Sites, 1996)
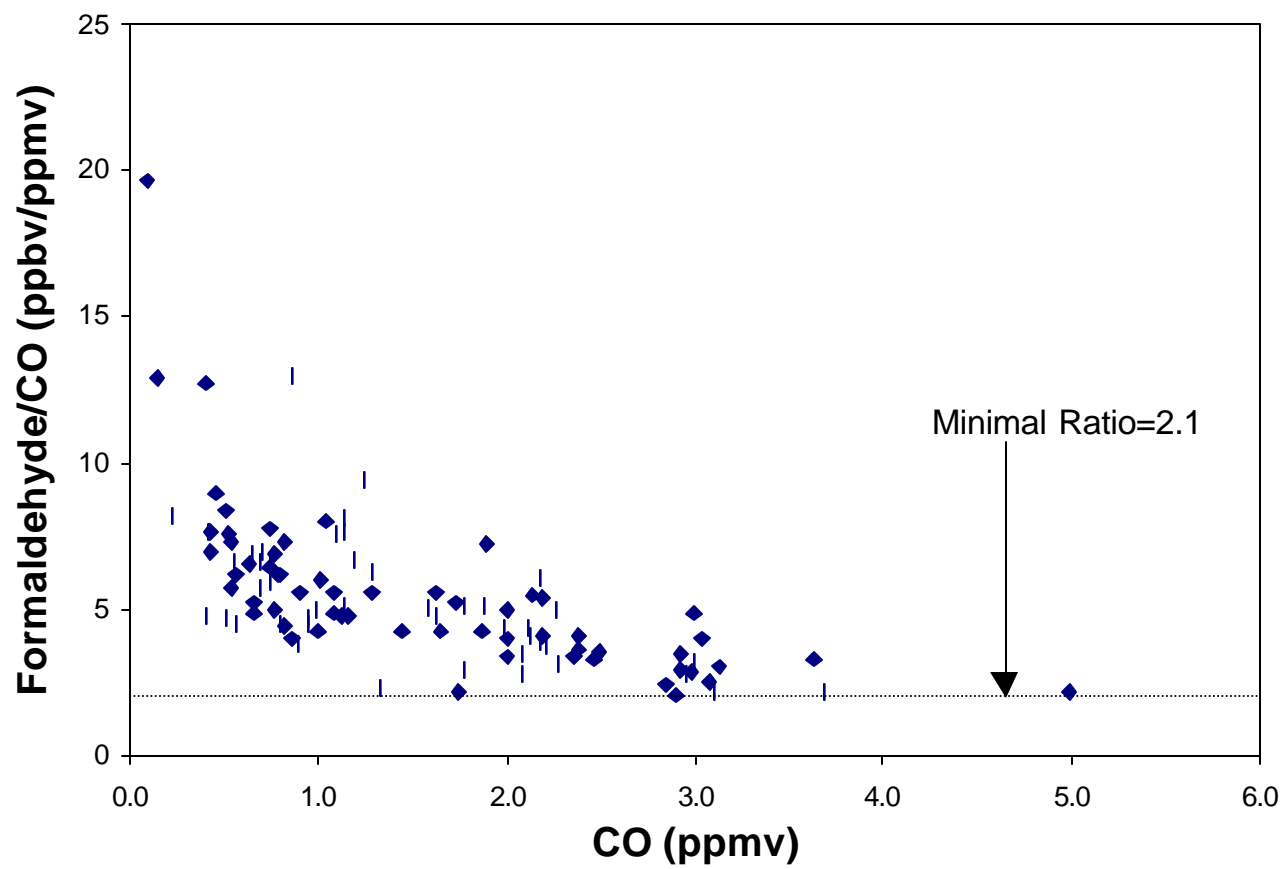
Figure 11. Formaldehyde/CO Ratio versus CO for SoCAB (Three DRI Sites, 1996)

SoCAB (TAC Winter Data, 1996 and 1997)
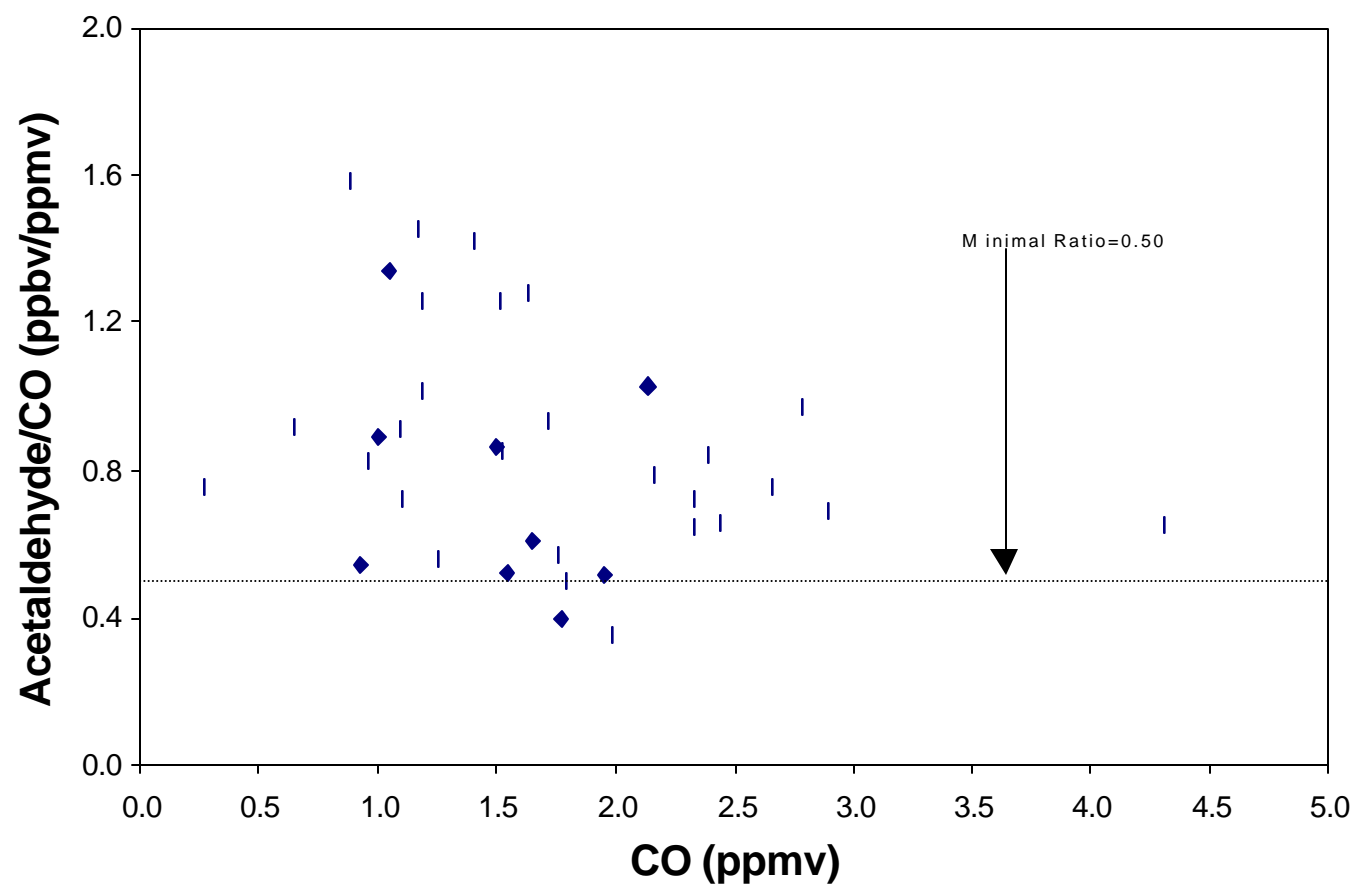
Figure 12. Acetaldehyde/CO Ratio versus CO for SoCAB (TAC Winter Data, 1996 and 1997).

SoCAB (Three DRI Sites, 1996)
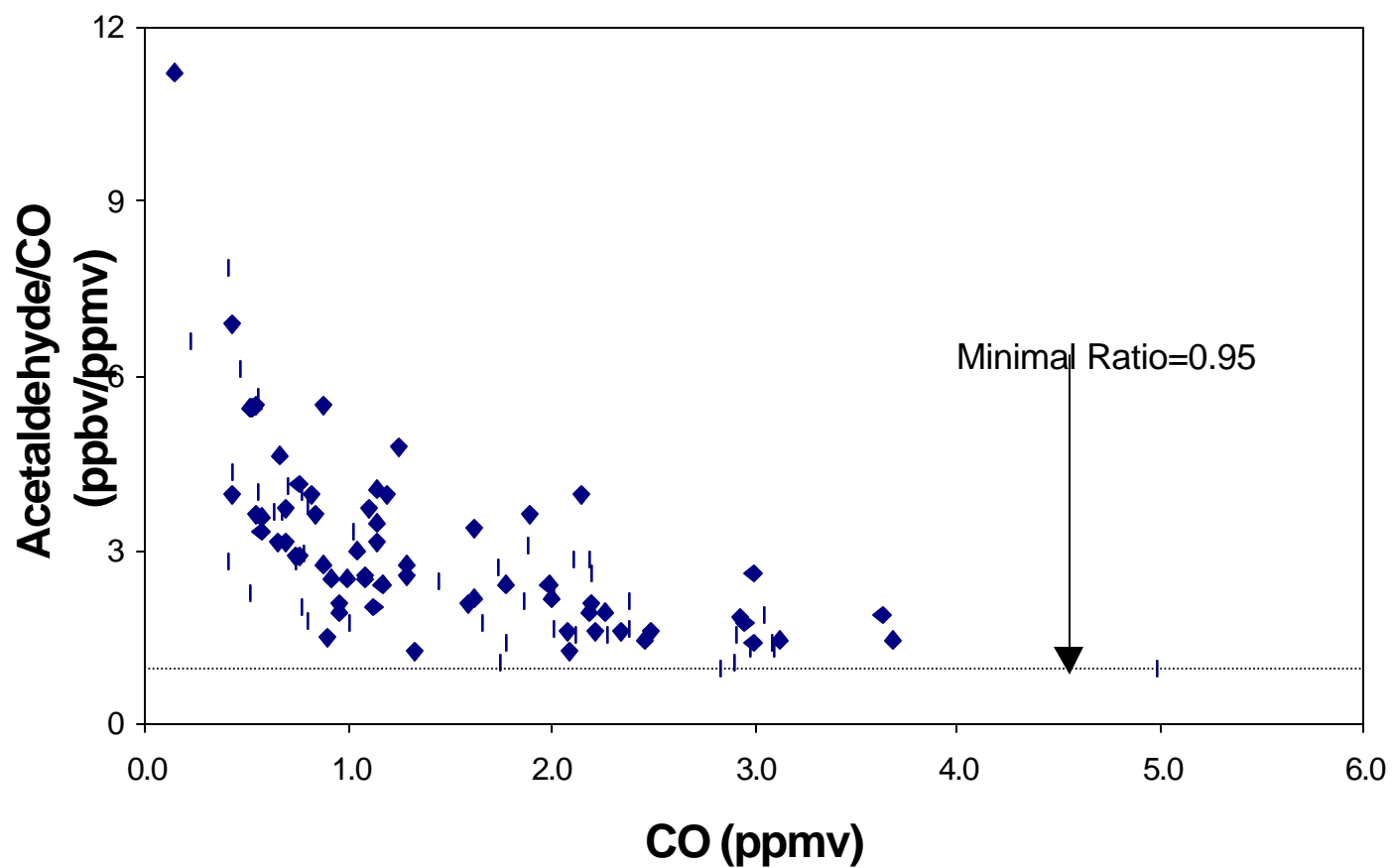
Figure 13. Acetaldehyde/CO Ratio versus CO for SoCAB (Three DRI Sites, 1996).

of 0.1 ppm CO and 0.5 ppb acetaldehyde or formaldehyde from the measured values. These background values were determined from measurements at Santa Catalina, Point Conception and San Nicholas Island.

To determine a factor relating aldehydes to oxidant, we assembled carbon monoxide and oxidant (O_3+NO_2) data to match aldehyde measurements from the toxics monitoring network in the SoCAB. First, we used the aldehyde to CO ratios determined above to estimate primary acetaldehyde. Then we subtracted this from the measured aldehyde value to obtain a residual aldehyde amount (presumably secondary in origin). Then we plotted the residual aldehyde vs. oxidant, after subtracting a background value of .03 ppm oxidant. This background value was determined by looking at the distribution of oxidant values measured in the South Coast Air Basin between 1996 and 1998. More than 98.6 % of the measured daily average values were .03 ppm or higher. Using the acetaldehyde to CO ratio of 0.50, a best fit oxidant slope was determined to be 40 for the TAC data. Using the ratio of 0.95 from the DRI data, the best fit oxidant slope for TAC data was determined to be 31. Using the formaldehyde to CO ratio of 1.4, a best fit oxidant slope was determined to be 73 for the TAC data. Using the ratio of 2.1 from the DRI data, the best fit oxidant slope for TAC data was determined to be 80. For residual acetaldehyde our R^2 regression coefficients were .50 to .54, depending on which slope factors were used. For residual formaldehyde our R^2 regression coefficients were .12 to .37, depending on which slope factors were used. When we tried applying the CO and Oxidant ratios to predict daily aldehyde values, the maximum predicted values at the toxics monitoring sites in the SoCAB on actual sampling days were 75% or more higher than measured maximum values. Therefore, we decided that this approach did not provide sufficiently reliable estimates to use in our analysis.

3.2.3 Toluene, Xylenes, Isobutene and n-Hexane

OEHHA requested information on annual exposure and maximum one-hour concentrations for toluene, xylenes, isobutene, and n-hexane. In response to this, we did a sensitivity evaluation of 1997 levels for these compounds. A key part of the sensitivity evaluation involved developing ratios between the compounds of interest and CO. This is discussed below, followed by estimates of 1997 pollutant levels.

After reviewing the estimated 1997 concentrations relative to chronic Reference Exposure Levels (RELs), OEHHA concluded that even a few fold difference in concentration from the use of one fuel over the other is not going to be a significant health concern. This was because current levels of these compounds are one to two orders of magnitude below their chronic RELs. Thus, airshed modeling analysis was not performed to predict future air quality levels of these compounds.

3.2.3.1 Ratio Between Compounds and CO

Following a procedure similar to that described in section 3.2.1.1, we developed ratios between the compounds of interest and CO. The results for each of the compounds evaluated follow:

3.2.3.1.1 Toluene

Table 4 summarizes the ratios and correlation coefficients between toluene and CO derived from TAC data, DRI data, Sepulveda data, and the emission inventory. This includes ratios derived from each monitoring site as well as sites combined (basin-wide) in the same data set. In general, good correlation was observed in all cases except the Riverside site. The ratios derived from air quality data range from 2.3 to 4.6.

3.2.3.1.2 Combined meta and para Xylenes

Table 5 summarizes the ratios and correlation coefficients between combined meta and para xylenes (m&p-xylene) and CO derived from the same data sets. In general, good correlation was observed for all data sets. The ratios obtained range from 1.1 to 1.9.

Table 4. Linear Regression Parameters for Correlations between Ambient Levels of Toluene and CO[a].

	TAC Network		DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventory[b]	
	Ratio	R^2	Ratio	R^2	Ratio	R^2	Ratio	R^2	All Sources	On-road Sources
1996										
South Coast Air Basin[c]	2.73	0.84	3.91	0.82	3.96	0.78			3.74	
Burbank	2.84	0.85	4.26	0.94	4.35	0.89				
Los Angeles	2.55	0.82	3.24	0.89	3.29	0.86				
Long Beach	2.77	0.86								
Riverside	3.11	0.31								
Azusa			4.56	0.88	4.57	0.77				
Sepulveda Tunnel							2.27	0.95		
Caldecott Tunnel										
1997										
South Coast Air Basin[c]	2.49	0.76								
Burbank	2.66	0.65								
Los Angeles	2.36	0.80								
Long Beach	2.55	0.75								
Caldecott Tunnel										

a. Concentration units are ppmv for CO and ppbv for toluene. CO background of 100 ppb was subtracted in CO measurements.
   Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.
b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.
c. Basin-wide ratio and correlation coefficient were calculated using the data collected in the SoCAB.

Table 5. Linear Regression Parameters for Correlations between Ambient Levels of m&p-Xylene and CO[a].

	TAC Network		DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventory[b]	
	Ratio	R^2	Ratio	R^2	Ratio	R^2	Ratio	R^2	All Sources	On-road Sources
1996										
South Coast Air Basin[c]	1.29	0.93	1.83	0.87	1.76	0.85			1.33	
Burbank	1.27	0.91	1.90	0.91	1.85	0.94				
Los Angeles	1.31	0.96	1.68	0.82	1.63	0.84				
Long Beach	1.38	0.82								
Riverside	1.32	0.67								
Azusa			2.00	0.91	1.88	0.79				
Sepulveda Tunnel							1.33	0.97		
Caldecott Tunnel										
1997										
South Coast Air Basin[c]	1.15	0.84								
Burbank	1.16	0.62								
Los Angeles	1.15	0.92								
Long Beach	1.13	0.88								
Caldecott Tunnel										

a. Concentration units are ppmv for CO and ppbv for m&p-xylene. CO background of 100 ppb was subtracted in CO measurements. Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.

b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.

c. Basin-wide ratio and correlation coefficient were calculated using the data collected in the SoCAB.

3.2.3.1.3   o-Xylene

Table 6 summarizes the ratios and correlation coefficients between o-xylene and CO derived from the same data sets. In general, good correlation was observed for all data sets. The ratios obtained range from 0.4 to 1.8.

3.2.3.1.4   Isobutene

Table 7 summarizes the ratios and correlation between isobutene and CO derived from DRI data, the Sepulveda tunnel study, and the emission inventory. This compound is not measured in our TAC network. In general, good correlation was observed for all data sets except Los Angeles. The ratios derived range from 0.9 to 1.6.

3.2.3.1.5   n-Hexane

Table 8 summarizes the ratios and correlation coefficients between n-hexane and CO derived from DRI data, the Sepulveda tunnel study, and the emission inventory. Like isobutene, n-hexane is not measured in our TAC network. In general, good correlation was observed for all data sets. The ratios derived range from 0.5 to 1.0.

3.2.3.2   Estimated 1997 Concentrations
We made estimates of expected maximum annual-average and maximum one-hour average concentrations for toluene, m&p-xylene, o-xylene, isobutene and n-hexane. These were done using available measurements from the toxics monitoring network and by establishing a ratio to carbon monoxide and multiplying that ratio by maximum CO concentrations.

3.2.3.2.1   Estimated Maxima Using Ratio to CO

We calculated ranges of maximum annual-average and one-hour toxics compound levels using maximum measured CO levels in the South Coast Air Basin for 1996-1998 and the range of ratios to CO established in Section 3.2.3.1. The maximum annual-average and one-hour CO levels were both measured at Lynwood in 1996 and are 2.49 ppm and 22.5 ppm, respectively. The calculated maxima for the various compounds are shown in Table 9.

Table 6. Linear Regression Parameters for Correlations between Ambient Levels of o-Xylene and CO[a].

	TAC Network		DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventory[b]	
	Ratio	R^2	Ratio	R^2	Ratio	R^2	Ratio	R^2	All Sources	On-road Sources
1996										
South Coast Air Basin [c]	0.46	0.96	0.66	0.89	0.64	0.87			0.54	
Burbank	0.46	0.98	0.69	0.92	0.67	0.95				
Los Angeles	0.45	0.97	0.60	0.85	0.59	0.87				
Long Beach	0.48	0.87								
Riverside	0.49	0.72								
Azusa			0.73	0.92	0.70	0.83				
Sepulveda Tunnel							1.79	0.97		
Caldecott Tunnel										
1997										
South Coast Air Basin [c]	0.41	0.84								
Burbank	0.41	0.67								
Los Angeles	0.42	0.93								
Long Beach	0.39	0.70								
Caldecott Tunnel										

a. Concentration units are ppmv for CO and ppbv for o-xylene. CO background of 100 ppb was subtracted in CO measurements.
   Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.
b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.
c. Basin-wide ratio and correlation coefficient were calculated using the data collected in the SoCAB.

Table 7. Linear Regression Parameters for Correlations between Ambient Levels of Isobutene and CO[a].

	TAC Network		DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventory[b]	
	Ratio	R^2	Ratio	R^2	Ratio	R^2	Ratio	R^2	All Sources	On-road Sources
1996										
South Coast Air Basin[c]			1.05	0.54	0.95	0.62			1.24	
Burbank			1.11	0.68	0.99	0.68				
Los Angeles			0.97	0.40	0.96	0.54				
Long Beach										
Riverside										
Azusa			1.10	0.58	0.89	0.61				
Sepulveda Tunnel							1.55	0.92		
Caldecott Tunnel										
1997										
South Coast Basin-wide										
Burbank										
Los Angeles										
Long Beach										
Caldecott Tunnel										

a. Concentration units are ppmv for CO and ppbv for isobutene. CO background of 100 ppb was subtracted in CO measurements. Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.

b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.

c. Basin-wide ratio and correlation coefficient were calculated using the data collected in the SoCAB.

Table 8. Linear Regression Parameters for Correlations between Ambient Levels of n-Hexane and CO[a].

	TAC Network		DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventory[b]	
	Ratio	R^2	Ratio	R^2	Ratio	R^2	Ratio	R^2	All Sources	On-road Sources
1996										
South Coast Air Basin[c]			0.87	0.58	0.91	0.62			1.22	
Burbank			0.96	0.73	1.02	0.65				
Los Angeles			0.70	0.60	0.74	0.71				
Long Beach										
Riverside										
Azusa			1.03	0.73	1.03	0.74				
Sepulveda Tunnel							0.49	0.92		
Caldecott Tunnel										
1997										
South Coast Air Basin[c]										
Burbank										
Los Angeles										
Long Beach										
Caldecott Tunnel										

a. Concentration units are ppmv for CO and ppbv for n-hexane. CO background of 100 ppb was subtracted in CO measurements.
   Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.
b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.
c. Basin-wide ratio and correlation coefficient were calculated using the data collected in the SoCAB.

Table 9. Estimated Maximum Annual and One-hour Toxics Levels using CO as a Surrogate.

Compounds	Annual-average (ppbv)	One-hour Average (ppbv)
Toluene	6-11	52-104
M&p-Xylene	2.7-4.5	25-43
o-Xylene	1.0-4.5	9-41
Isobutene	2.2-4.0	20-36
n-Hexane	1.2-2.5	11-23

3.2.3.2.2 *Maximum One-hour Averages Extrapolated from Maximum Daily Averages*

We estimated the maximum one-hour values by extrapolating from measured maximum daily values. For toluene and o-xylene the measured maximum daily values for 1996-1997 in the South Coast Air Basin were 19 ppb and 3.5 ppb, respectively and were measured at Burbank on 1/10/96. For m&p-xylene the maximum daily value was 14.27 ppb, measured on 1/10/96 at Los Angeles-North Main. We used measured CO daily and maximum one-hour CO values at Burbank and Los Angeles on 1/10/96 to extrapolate to maximum one-hour toxics level assuming proportionality between CO and toxics levels at each location. At Burbank the daily and maximum one-hour CO levels were 7.43 ppm and 11.6 ppm, respectively. The calculated maximum one-hour average toluene and o-xylene levels are 29.7 ppb and 5.5 ppb. At Los Angeles the daily and maximum one-hour CO levels were 7.0 ppm and 10.3 ppm, respectively. The calculated maximum one-hour m&p-xylene level is 14.3 ppb. Isobutene and n-hexane are not measured as part of the TAC monitoring program, and no estimates were made for these two compounds.

3.2.3.2.3 *Maximum Measured Annual Average*

Based on TAC data for 1996-1997, the maximum measured annual-averages for the South Coast Air Basin were measured at Burbank in 1996 and were 5.12 ppb for toluene, 2.2 ppb for m&p-xylene, and 0.77 ppb for o-xylene.

3.3 Ethanol

The only ethanol air quality data readily available were those collected by DRI in the summers of 1995 and 1996. We used the 1996 data as the basis for estimating representative population weighted annual and maximum daily average and maximum one-hour average for 1997. The 1995 data were not used because cleaner burning gasoline was not widely available until 1996. The highest ethanol concentrations are expected in winter. Given only summer data, it was challenging to estimate concentrations in a different season. We opted to use CO as an index of mixing and dispersion to extrapolate from measured maximum ethanol concentrations in the summer to a different season.

Similar to other pollutants, we attempted to correlate ethanol with CO. The results, summarized in Table 10, showed poor correlation. This was not surprising, given that on-road vehicles currently emit less than one percent of the estimated ethanol emissions in the South Coast Air Basin (see Appendix ??).

Table 10. Linear Regression Parameters for Correlations between Ambient Levels of Ethanol and CO[a].

	TAC Network		DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventory[b]	
	Ratio	R^2	Ratio	R^2	Ratio	R^2	Ratio	R^2	All Sources	On-road Sources
1996										
South Coast Air Basin[c]			4.55	0.22	4.43	0.27			3.75	0.04
Burbank			4.25	0.12	4.32	0.23				
Los Angeles			4.37	0.17	4.34	0.23				
Long Beach										
Riverside										
Azusa			5.27	0.35	4.71	0.34				
Sepulveda Tunnel										
Caldecott Tunnel										
1997										
South Coast Air Basin[c]										
Burbank										
Los Angeles										
Long Beach										
Caldecott Tunnel										

a. Concentration units are ppmv for CO and ppbv for ethanol. CO background of 100 ppb was subtracted in CO measurements.
   Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.
b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.
c. Basin-wide ratio and correlation coefficient were calculated using the data collected in the SoCAB.

3.3.1 Maximum Daily Average

The maximum daily average ethanol concentration is expected to occur in winter, and was calculated using one procedure with two different assumptions. The general equation for calculating the maximum daily average is as follows:

$$\text{Ethanol (Max 24hr)} = \text{Ethanol(Hi 6hr Ave.)} \times \frac{\dfrac{\text{Annual Maximum 24hr Avg. CO}}{\text{Winter CO Emissions}}}{\dfrac{\text{Summer Matching 6hr CO Air Quality}}{\text{Summer CO Emission}}}$$

This procedure was applied two ways --once using only data for Los Angeles (the monitoring site with the highest ethanol measurements), and once using the CO data for Lynwood (the site with the highest CO levels) and ethanol data for Los Angeles. The latter application was made attempting to represent conditions of very limited mixing/dispersion that occur at Lynwood. A maximum daily average ethanol concentration of 47 ppb was calculated using the Los Angeles maximum as follows:

$$\text{Ethanol (Max 24hr)} = 25.7 \text{ ppb} \times \frac{\dfrac{7.0 \text{ ppm}}{6520 \text{ tons/day}}}{\dfrac{3.10 \text{ ppm}}{5283 \text{ tons/day}}} = 47 \text{ ppb}$$

A similar calculation yielded 51 ppb using Lynwood CO data. In the equation above, the CO air quality levels are divided by the relevant seasonal (winter or summer) emission estimates to adjust for the effects of higher CO emissions in winter. This is because CO is being used as an index of dispersion and mixing under the assumption that CO emissions are kept constant.

3.3.2 Maximum one-hour Average

The maximum one-hour average ethanol concentration is expected to occur in winter and was calculated using one procedure with two different assumptions. The general equation for calculating the maximum one-hour average is as follows:

$$\text{Ethanol (Max 1hr)} = \text{Ethanol (Hi 3hr Ave.)} \times \frac{\dfrac{\text{Annual Maximum 1hr Avg. CO}}{\text{Winter CO Emissions}}}{\dfrac{\text{Summer Matching 3hr CO Air Quality}}{\text{Summer CO Emissions}}}$$

This procedure was applied two ways --once using only data for Los Angeles (the monitoring site with the highest ethanol measurements), and once using the maximum one-hour average CO from Lynwood (the site with the highest CO levels) and the rest of the data from Los Angeles. The latter application was made attempting to represent conditions of very limited mixing/dispersion that occur at Lynwood. A maximum one-hour average ethanol concentration of 78 ppb was calculated using the Los Angeles maximum as follows:

$$\text{Ethanol (Max 1hr)} = 37.0 \text{ ppb} \times \frac{\dfrac{10.3 \text{ ppm}}{6520 \text{ tons/day}}}{\dfrac{3.97 \text{ ppm}}{5283 \text{ tons/day}}} = 78 \text{ ppb}$$

A similar calculation yielded 108 ppb using Lynwood CO data.

3.3.3 Population Weighted Annual Exposure

There were three sites for which data were collected in the DRI study -- Azusa, Burbank and Los Angeles -North Main. For each site, an estimated annual-average ethanol concentration was calculated using carbon monoxide concentrations as an index of ventilation and dispersion. The following equation was used:

$$\text{Ethanol (Annual)} = \text{Ethanol (Summer 1996 Avg.)} \times \frac{\dfrac{\text{Annual CO Air Quality}}{\text{Annual CO Emissions}}}{\dfrac{\text{Summer 1996 CO Air Quality}}{\text{Summer CO Emissions}}}$$

The time period for averaging the 1996 Summer CO data was 6-9 A.M. and 1-4 P.M. daylight time for July 7, 1996 through September 29, 1996. This corresponds to the time period over which the DRI ethanol data were collected. Applying the above equation to Burbank data, we obtain:

$$\text{Ethanol (Annual)} = 5.35 \text{ ppb} \times \frac{\dfrac{1.705 \text{ ppm}}{5782 \text{ tons/day}}}{\dfrac{1.651 \text{ ppm}}{5283 \text{ tons/day}}} = 5.04 \text{ ppb}$$

The population weighted annual-average concentration was calculated using annual-average data for the three monitoring sites and the procedure described in section 3.2.1.2.3 above. The population weighted annual-average concentration calculated to represent the South Coast Air Basin in 1997 is 5.4 ppb ethanol.

3.4 Alkylates

Similar to the analysis performed for toluene, we also did a sensitivity evaluation of 1997 concentrations for four alkylates. Alkylates is a class of compounds that is present in motor vehicle fuels. Based on the measurements by DRI in the SoCAB in 1996, there were over 30 alkylates observed in the atmosphere. The top four alkylates in terms of their average concentration were 2-methylpentane (2.11 ppb), 3-methylpentane (1.24 ppb), methylcyclopentane (1.33 ppb), and 2,2,4-trimethylpentane (1.31 ppb). We used the DRI data and measured CO levels in 1996-1998 to estimate annual-average and maximum one-hour alkylate concentrations, using a procedure similar to that in section 3.2.3, used for isobutene and n-hexane. Below we discuss first the development of ratios between the various compounds and CO, and then estimated 1997 pollutant concentrations.

We provided the 1997 estimated pollutant concentrations for these compounds to OEHHA. Airshed modeling analysis to predict future air quality levels of these compounds will not be undertaken unless OEHHA responds that these compounds or other alkylates constitute a significant health concern.

3.4.1 Ratio between Compounds and CO

Following a procedure similar to that described in section 3.2.1.1, we developed ratios between the compounds of interest and CO. Both DRI data and Sepulveda Tunnel data were used in our analysis. Alkylates are not measured in the TAC monitoring network. The results are presented below.

3.4.1.1 2-Methylpentane

Table 11 summarizes the ratios and correlation coefficients between 2-methylpentane and CO derived from DRI data and Sepulveda data. Good correlation was observed for all data sets. The ratios obtained range from 1.2 to 1.7.

3.4.1.2 3-Methylpentane

Table 12 summarizes the ratios and correlation coefficients between 3-methylpentane and CO derived from DRI data and Sepulveda data. Good correlation was observed for all data sets. The ratios obtained range from 0.7 to 1.0.

3.4.1.3 Methylcyclopentane

Table 13 summarizes the ratios and correlation coefficients between methylcyclopentane and CO derived from DRI data and Sepulveda data. Good correlation was observed for all data sets. The ratios obtained range from 0.8 to 1.2.

3.4.1.4 2,2,4-Trimethylpentane

Table 14 summarizes the ratios and correlation coefficients between 2,2,4-trimethylpentane and CO derived from DRI data and Sepulveda data. Good correlation was observed for all data sets. The ratios obtained range from 0.8 to 1.1.

3.4.2 Estimated 1997 Concentrations

We made estimates of expected maximum annual-average and maximum one-hour average concentrations for 2-methylpentane, 3-methylpentane, methylcyclopentane, and 2,2,4-trimethylpentane. These were done by using maximum measured CO levels in the SoCAB from 1996-1998 and the range of ratios to CO established above. The maximum annual-average and one-hour CO levels, both measured at Lynwood in 1996, are 2.49 and 22.5 ppm, respectively. The calculated maxima for the alkylates are shown in Table 15.

Table 11. Linear Regression Parameters for Correlations between Ambient Levels of 2-Methylpentane and CO[a].

	TAC Network		DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventory[b]	
	Ratio	R^2	Ratio	R^2	Ratio	R^2	Ratio	R^2	All Sources	On-road Sources
1996										
South Coast Air Basin[c]			1.57	0.85	1.60	0.84				
Burbank			1.71	0.97	1.71	0.97				
Los Angeles			1.39	0.75	1.43	0.82				
Long Beach										
Riverside										
Azusa			1.70	0.91	1.73	0.80				
Sepulveda Tunnel							1.17	0.95		
Caldecott Tunnel										
1997										
South Coast Air Basin[c]										
Burbank										
Los Angeles										
Long Beach										
Caldecott Tunnel										

a. Concentration units are ppmv for CO and ppbv for 2-methylpentane. CO background of 100 ppb was subtracted in CO measurements.
   Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.
b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.
c. Basin-wide ratio and correlation coefficient were calculated using the data collected in the SoCAB.

Table 12. Linear Regression Parameters for Correlations between Ambient Levels of 3-Methylpentane and CO[a].

	TAC Network		DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventory[b]	
	Ratio	R^2	Ratio	R^2	Ratio	R^2	Ratio	R^2	All Sources	On-road Sources
1996										
South Coast Air Basin[c]			0.94	0.85	0.95	0.84				
Burbank			1.02	0.98	1.02	0.96				
Los Angeles			0.82	0.77	0.84	0.82				
Long Beach										
Riverside										
Azusa			1.03	0.89	1.03	0.80				
Sepulveda Tunnel							0.69	0.95		
Caldecott Tunnel										
1997										
South Coast Air Basin[c]										
Burbank										
Los Angeles										
Long Beach										
Caldecott Tunnel										

a. Concentration units are ppmv for CO and ppbv for 3-methylpentane. CO background of 100 ppb was subtracted in CO measurements.
   Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.
b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.
c. Basin-wide ratio and correlation coefficient were calculated using the data collected in the SoCAB.

Table 13. Linear Regression Parameters for Correlations between Ambient Levels of Methylcyclopentane and CO[a].

	TAC Network		DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventory[b]	
	Ratio	R^2	Ratio	R^2	Ratio	R^2	Ratio	R^2	All Sources	On-road Sources
1996										
South Coast Air Basin[c]			1.05	0.85	1.04	0.86				
Burbank			1.13	0.96	1.11	0.96				
Los Angeles			0.92	0.77	0.94	0.82				
Long Beach										
Riverside										
Azusa			1.15	0.90	1.11	0.86				
Sepulveda Tunnel							0.76	0.95		
Caldecott Tunnel										
1997										
South Coast Air Basin[c]										
Burbank										
Los Angeles										
Long Beach										
Caldecott Tunnel										

a. Concentration units are ppmv for CO and ppbv for methylcyclopentane. CO background of 100 ppb was subtracted in CO measurements.
   Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.
b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.
c. Basin-wide ratio and correlation coefficient were calculated using the data collected in the SoCAB.

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Table 14. Linear Regression Parameters for Correlations between Ambient Levels of 2,2,4-Trimethylpentane and CO[a].

	TAC Network		DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventory[b]	
	Ratio	R^2	Ratio	R^2	Ratio	R^2	Ratio	R^2	All Sources	On-road Sources
1996										
South Coast Air Basin[c]			0.97	0.87	0.98	0.76				
Burbank			1.05	0.95	1.06	0.94				
Los Angeles			0.83	0.89	0.84	0.91				
Long Beach										
Riverside										
Azusa			1.10	0.93	1.12	0.61				
Sepulveda Tunnel							0.80	0.94		
Caldecott Tunnel										
1997										
South Coast Air Basin[c]										
Burbank										
Los Angeles										
Long Beach										
Caldecott Tunnel										

a. Concentration units are ppmv for CO and ppbv for 2,2,4-trimethylpentane. CO background of 100 ppb was subtracted in CO measurements. Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.

b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.

c. Basin-wide ratio and correlation coefficient were calculated using the data collected in the SoCAB.

Table 15. Estimated Maximum Annual and One-hour Average Alkylate Concentrations Using CO as a Surrogate

Compounds	Annual-average (ppbv)	One-hour Average (ppbv)
2-MethylPentane	3.0-4.2	27-38
3-Methylpentane	1.7-2.5	16-23
Methylcyclopentane	2.0-3.0	18-27
2,2,4-Trimethylpentane	2.0-2.7	18-25

4 Methods to Estimate Future Air Quality Levels

4.1 Basic Procedure for all Pollutants

Future Air Quality Levels were estimated using estimated 1997 concentrations (Section 3) and results from the photochemical simulation model for the specific pollutant of concern. Unlike the 1997 estimates, we did not use correlations between CO and toxics compounds to estimate future year concentrations. Separate model simulations were made using MTBE fuel for 1997 and 2003, 2.0 percent oxygen ethanol fuel (ET20) in 2003, 3.5 percent oxygen ethanol fuel (ET35) in 2003, non-oxygenated fuel (UNOX) in 2003. Additionally, simulations for ET20 and ET35 were made using a special species profile specified by Harley. These runs were designated ET20H and ET35H. Although the model simulation covered 3 days, the only day deemed suitable for comparison was the third day. This was because results on the first and second day were believed to be strongly affected by the choice of initial conditions. The general procedure for calculating future air quality was:

$$\text{Future Air Quality for Fuel X} = 1997 \text{ Air Quality x } \frac{\text{Modeled Air Quality for Fuel X}}{\text{Modeled Air Quality for 1997}}$$

Departures from this basic procedure are discussed in Sections 4.2 and 4.3.

4.1.1 Maximum Daily Average

For estimating future maximum daily average concentrations, we normally used the maximum daily average concentration for the highest grid in the gridded modeling region for the 3rd day of the model simulation as the model air quality parameter in the equation above. Notable exceptions are estimates for benzene, carbon monoxide, and MTBE, where we used the modeled daily average for the grid cell containing Lynwood, the monitoring site with the highest measured CO values. The use of the Lynwood grid cell values was because it yielded higher future concentrations than if the gridded region maximum daily average was used. For 1,3-butadiene, the ratio of model results for the grid cell containing Lynwood was lower than the ratio of gridded region maxima. Thus, 1,3-butadiene was not treated as an exception.

4.1.2 Maximum one-hour Average

For estimating future maximum one-hour average concentrations we normally used the maximum one-hour average concentration in the gridded modeling region for the 3rd day of the model simulation as the model air quality parameter in the equation above. Notable exceptions are estimates for benzene, carbon monoxide, and MTBE where we used the modeled maximum one-hour average for the grid cell

containing Lynwood, the monitoring site with highest CO values. The use of the Lynwood grid cell values was because it yielded higher future concentrations than if the gridded region maximum one-hour average was used. For 1,3-butadiene, the ratio of model results for the grid cell containing Lynwood was lower than the ratio of gridded region maxima. Thus, 1,3-butadiene was not treated as an exception.

4.1.3 Population Weighted Annual-average Exposure

For the population weighted annual-average exposure, we normally used the region-wide population weighted average of the daily average model results for the 3rd day of the model simulation as the model air quality parameter in the equation above. This was believed reasonable for any compound that is a primary pollutant. Acetaldehyde and formaldehyde have substantial contributions from secondary reactions in the atmosphere and were treated differently as discussed below.

4.2 Special Procedures for Criteria Pollutants

Generally we followed the basic procedures for estimating future air quality levels except as follows:

For maximum daily and maximum one-hour average values, we used the model values for the grid cell containing Lynwood, as discussed above. For estimating future maximum eight-hour average CO and ozone concentrations we used maximum eight-hour average model results and for CO, used model values for the grid cell containing Lynwood.

4.3 Special Procedures for Toxic Pollutants

Generally we followed the basic procedures for estimating future air quality levels except as follows:

For maximum daily and maximum one-hour average values for benzene and MTBE, we used the model values for the grid cell containing Lynwood, as discussed above.

For acetaldehyde and formaldehyde we used the basic procedure for the maximum daily and maximum one-hour averages. This was deemed reasonable because in 1997 the maximum daily and maximum one-hour concentrations occurred in August, the month of the model simulation. For the population weighted annual-average a different procedure was needed because the contribution from primary emission sources vs. secondary formation in the atmosphere was expected to be different in different seasons of the year. The basic equation for estimating future year aldehydes was as follows:

$$
\begin{aligned}
\text{Future Air Quality} = {} & 1997\,\text{Primary Air Quality} \times \frac{\text{Modeled Future Primary Air Quality}}{\text{Modeled 1997 Primary Air Quality}} \\
& + 1997\,\text{Secondary Air Quality} \times \frac{\text{Modeled Future Secondary Air Quality}}{\text{Modeled 1997 Secondary Air Quality}}
\end{aligned}
$$

This requires that the amount of primary and secondary aldehyde be known for 1997 and for the model results. The model was set up so secondary aldehydes were tracked separately from primary aldehydes. The 1997 Primary Air Quality and 1997 Secondary Air Quality were determined from 1996-1997 aldehyde and CO data using the following procedure:

#1. Determine primary aldehyde/CO ratio representative of 1997 -- This was done in Section 3.2.2.2
#2. Determine average CO for month using all CO measurements at monitoring site
#3. Determine average CO for site/month using just aldehyde sampling days
#4. Determine average aldehyde (acetaldehyde or formaldehyde) for site/month
#5. Estimate average primary aldehyde by month = #1 * #2 unless this exceeds (#4 / #3) * #2, in which case substitute (#4 / #3) * #2
#6. Estimate average secondary aldehyde by month =((#4 - (#1 * #3)) / #3) * #2 ; unless #1 * #2 exceeds (#4 / #3) * #2, in which case substitute zero

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#7. Estimate annual-average primary aldehyde = #5 averaged over 12 months of the year

#8. Estimate annual-average secondary aldehyde = #6 averaged over 12 months of the year

This procedure was applied using separately the DRI based and Toxics Monitoring Network based aldehyde to CO ratios developed in Section 3.2.2.2. To obtain population weighted results, future aldehyde values were estimated for the four monitoring locations where both aldehydes and CO are measured, and then these values were population weighted.

5   Results

The resulting air quality estimates for 1997 and the different fuel scenarios in 2003 are shown in Table 16. In general, the table shows the estimated population weighted annual exposure, maximum daily average and maximum one-hour average for benzene, butadiene, acetaldehyde, formaldehyde, carbon monoxide, nitrogen dioxide, ozone, PM_{10}, ethanol, and MTBE. In some cases the pollutant averaging times are adjusted to show different averaging times. For example, maximum eight-hour averages instead of maximum daily average are included for carbon monoxide and ozone since there are eight-hour standards for these two pollutants. In addition, the maximum predicted model one-hour and daily average concentrations for PAN and peroxypropionyl nitrate (PPN) are included for 1997 and the various 2003 fuel scenarios. A column on the table indicates whether each row of the table was used (Y) or was not used (N) in producing summaries of the estimated maximum pollutant levels. Two reasons that a particular row may not have been used in a summary are that it reflected summer values and winter values were higher, or that it reflected 1997 model results that were lower than estimated 1997 maximum values.

Table 16. Estimated Pollutant Levels in the South Coast Air Basin

	Used for Range?	1997 MTBE	2003 MTBE	2003 Et2%	2003 Et2%H	2003 Et3.5%	2003 Et3.5%H	2003 NonOxy	Comments
Benzene, ppbV									
Population Weighted Annual Exposure									
Based on Measured Values	Y	1.07	0.78	0.77	0.72	0.79	0.73	0.76	
Projected Level based on CO levels	Y	1.19	0.87	0.86	0.80	0.88	0.81	0.85	
Model Output Pop Wt Summer Daily	N	0.82	0.60	0.59	0.55	0.60	0.56	0.59	Summer
Maximum Daily Average									
Measured Daily Max.	Y	7.4	5.5	5.5	5.2	5.5	5.2	5.5	
Projected Maximum based on CO levels	Y	9.6	7.2	7.1	6.8	7.2	6.8	7.1	
Model Output - Lynwood	N	0.69	0.51	0.51	0.49	0.51	0.49	0.51	Summer
Maximum from Model Output	N	1.72	1.17	1.15	1.10	1.18	1.10	1.15	Summer
Maximum One-hour Average									
Extrapolated from Measured Daily Max.	Y	11.6	8.4	8.4	7.4	8.4	7.4	8.4	
Projected Maximum based on CO levels	Y	22.5	16.4	16.4	14.3	16.4	14.3	16.4	
Model Output - Lynwood	N	1.1	0.8	0.8	0.7	0.8	0.7	0.8	Summer
Maximum from Model Output	N	3.4	2.2	2.2	1.9	2.3	2.0	2.2	Summer
1,3-Butadiene, ppb									
Population Weighted Annual Exposure									
Based on Measured Values	Y	0.34	0.19	0.19	0.19	0.19	0.19	0.20	
Projected Level based on CO levels	Y	0.36	0.20	0.20	0.21	0.20	0.20	0.21	
Model Output Pop Wt Summer Daily	N	0.074	0.042	0.042	0.042	0.041	0.041	0.043	Summer
Maximum Daily Average									
Measured Daily Max.	Y	2.0	2.0	2.0	2.0	2.0	2.0	2.0	
Projected Maximum based on CO levels	Y	2.9	2.9	2.9	2.9	2.9	2.9	2.9	
Maximum from Model Output	N	0.879	0.879	0.879	0.879	0.875	0.875	0.879	Summer
Maximum One-hour Average									
Extrapolated from Measured Daily Max.	Y	3.1	3.1	3.1	3.1	3.1	3.1	3.1	
Projected Maximum based on CO levels	Y	6.8	6.8	6.8	6.8	6.8	6.8	6.8	
Maximum from Model Output	N	3.0	3.0	3.0	3.0	3.0	3.0	3.0	Summer
Acetaldehyde, ppbV									
Population Weighted Annual Exposure									
Based on Measured Values									
TAC Based Value and Projection	Y	1.75	1.51	1.56	1.55	1.70	1.69	1.53	
DRI/TAC Based Projection	Y		1.45	1.51	1.51	1.76	1.75	1.46	
Model Output Pop Wt Summer Daily	N	3.23	2.81	2.87	2.85	2.96	2.93	2.84	Summer
Maximum Daily Average									
Measured Daily Max.	Y	5.1	5.1	5.1	5.1	5.1	5.1	5.1	
Maximum from Model Output	Y	6.2	6.2	6.2	6.2	6.2	6.2	6.2	
Maximum One-hour Average									
Extrapolated from DRI Measured Three-hour Max.using O3	Y	17.7	16.7	16.9	16.9	17.1	17.1	16.9	
Extrapolated from Measured Daily Max.using O3	Y	13.8	13.1	13.2	13.2	13.4	13.4	13.2	
Maximum from Model Output	N	9.2	8.7	8.8	8.8	8.9	8.9	8.8	Summer

Formaldehyde	Used for Range?	1997 MTBE	2003 MTBE	2003 Et2%	2003 Et2%H	2003 Et3.5%	2003 Et3.5%H	2003 NonOxy	Comments
Population Weighted Annual Exposure									
Based on Measured Values									
TAC Based Value and Projection	Y	4.65	3.735	3.679	3.659	3.673	3.657	3.679	
DRI/TAC Based Projection	Y		3.640	3.588	3.575	3.573	3.563	3.581	
Model Output Pop Wt Summer Daily	N	6.85	5.97	5.88	5.85	5.90	5.86	5.88	Summer
Maximum Daily Average									
Measured Daily Max.	Y	14.0	12.2	12.2	12.0	12.2	12.1	12.2	
Maximum from Model Output	N	11.35	9.93	9.86	9.76	9.88	9.79	9.85	
Maximum One-hour Average									
Extrapolated from DRI Measured Three-hour Max.using O3	Y	20.3	20.7	20.4	20.4	20.5	20.5	20.4	
Extrapolated from Measured Daily Max.using O3	Y	37.8	38.5	38.0	38.0	38.1	38.1	38.0	
Maximum from Model Output	Y	22.7	23.1	22.8	22.8	22.9	22.9	22.8	
Carbon Monoxide, ppmV									
Maximum Eight-hour Average									
Measured Eight-hour Max.	Y	17.5	14.3	14.3	14.3	13.4	13.4	14.7	
Model Output - Lynwood	N	1.010	0.828	0.828	0.828	0.773	0.773	0.847	Summer
Maximum from Model Output	N	2.43	1.82	1.82	1.82	1.66	1.66	1.87	Summer
Maximum One-hour Average									
Measured One-hour Max., ppmV	Y	22.5	19.2	19.2	19.2	18.0	18.0	19.7	
Model Output - Lynwood	N	1.11	0.95	0.95	0.95	0.89	0.89	0.97	Summer
Maximum from Model Output	N	3.02	2.19	2.19	2.19	1.97	1.97	2.26	Summer
Nitrogen Dioxide, ppmV									
Maximum Annual Average Exposure									
Based on Measured Values	Y	0.043	Not estimated since no significant change in Max One-hour						
Maximum Daily Average									
Measured Daily Max.	Y	0.117	0.098	0.097	0.097	0.097	0.097	0.097	
Maximum from Model Output	N	0.073	0.061	0.061	0.061	0.060	0.060	0.061	Summer
Maximum One-hour Average									
Measured One-hour Max.	Y	0.255	0.235	0.235	0.235	0.235	0.235	0.235	
Maximum from Model Output	N	0.105	0.097	0.097	0.097	0.097	0.097	0.097	Summer
Ozone, ppbV									
Maximum Eight-hour Average									
Measured Eight-hour Max.	Y	0.206	0.196	0.197	0.196	0.196	0.195	0.198	
Maximum from Model Output	N	0.187	0.178	0.179	0.179	0.178	0.178	0.180	
Maximum One-hour Average									
Measured One-hour Max.	Y	0.244	0.231	0.232	0.230	0.229	0.228	0.234	
Maximum from Model Output	N	0.236	0.223	0.224	0.223	0.221	0.220	0.227	
Particulate Matter (10u or less)									
Maximum Annual Geometric Mean									
Based on Measured Values, ug/m^3	Y	56	No significant change expected among 2003 scenarios						
Maximum Daily Average									
Measured Daily Max., ug/m^3	Y	227	No significant change expected among 2003 scenarios						

	Used for Range?	1997 MTBE	2003 MTBE	2003 Et2%	2003 Et2%H	2003 Et3.5%	2003 Et3.5%H	2003 NonOxy	Comments
Ethanol, ppbV									
Population Weighted Annual Exposure									
Estimated from Summer Measurements	Y	5.4	5.1	8.2	7.0	11.3	8.8	5.1	Whole Year
Model Output Pop Wt Summer Daily	N	2.05	1.95	3.10	2.66	4.30	3.35	1.93	Summer
Maximum Daily Average									
Extrapolated Daily Summer Max.	N	21	19	20	20	21	20	19	Summer
Estimated Daily Winter Max.									
Lynwood	Y	51	46	48	48	50	49	46	Winter
LA-N Main	Y	47	43	45	44	46	45	43	Winter
Maximum from Model Output	N	19.05	17.34	18.04	17.79	18.66	18.14	17.34	Summer
Maximum One-hour Average									
Extrapolated One-hour Summer Max.	N	42	38	39	39	40	39	38	Summer
Estimated One-hour Winter Max.									
Lynwood	Y	108	98	101	100	103	101	98	Winter
LA-N Main	Y	78	71	73	72	75	73	71	Winter
Maximum from Model Output	N	45.6	41.4	42.5	42.1	43.6	42.8	41.4	Summer
MTBE									
Population Weighted Annual Exposure									
Based on Measured Values	Y	3.9	2.7	0	0	0	0	0	
Projected Level based on CO levels	Y	3.6	2.5	0	0	0	0	0	
Model Output Pop Wt Summer Daily	N	1.09	0.74	0	0	0	0	0	Summer
Maximum Daily Average									
Measured Daily Max., ppbV	Y	13	9	0	0	0	0	0	
Projected Maximum based on CO levels, ppbV	Y	29	21	0	0	0	0	0	
Model Output - Lynwood	N	0.97	0.69	0	0	0	0	0	Summer
Maximum from Model Output	N	2.63	1.74	0	0	0	0	0	Summer
Maximum One-hour Average									
Extrapolated from Measured Daily Max., ppbV	Y	19	13	0	0	0	0	0	
Projected Maximum based on CO levels, ppbV	Y	68	47	0	0	0	0	0	
Model Output - Lynwood	N	1.6	1.1	0	0	0	0	0	Summer
Maximum from Model Output	N	6.1	4.1	0	0	0	0	0	Summer
PAN, ppbV									
Maximum Daily Average									
Maximum from Model Output	Y	2.12	2.05	2.12	2.06	2.11	2.06	2.13	
Maximum One-hour Average									
Maximum from Model Output	Y	4.4	4.2	4.4	4.2	4.4	4.2	4.4	
PPN, ppbV									
Maximum Daily Average									
Maximum from Model Output	Y	0.579	0.579	0.604	0.596	0.571	0.571	0.613	
Maximum One-hour Average									
Maximum from Model Output	Y	1.4	1.4	1.4	1.4	1.4	1.4	1.5	

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